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Iron nano-particles for water treatment

Is the future free or fixed?

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Abstract

As global populations continue to increase, the pressure on water supplies will inevitably intensify. Consequently the international need for more efficient and cost effective water remediation technologies will also rise. The introduction of nano-technology into the industry may represent a significant advancement and zero-valent iron nano-particles (INPs) have been thoroughly studied for potential remediation applications. These nano-scale particles with metallic cores and oxide surfaces show broad applicability for treatment of both toxic organic compounds and heavy metals. However, the application of water dispersed INP suspensions is limited and somewhat contentious on the grounds of safety, whilst INP reaction mechanisms, oxide-fluid interactions, transport properties and ecotoxicity are areas still under investigation. Theoretically, the development of nano-composites containing INPs, or the less reactive iron oxide nano-particles (IONPs), to overcome these issues provides the logical next step for developing nano-materials that are better suited to wide application across the water industry. This chapter provides a thorough insight into the pros and cons of both mobile, dispersed INPs and static, bulk nano-composites; discussing the evolution of nano-technology for water treatment and the diverse range of products being developed whilst highlighting the limitations of individual solutions, overall classes of technology, and lack of comparative testing. The chapter discusses what further developments are needed to optimise remediation systems to subsequently achieve commercial maturity.

Keywords: Zero-valent iron, iron oxides, nano-particles, nano-composites, water remediation

1 Introduction

Water contamination is a major international problem caused by industrial, domestic and environmental influences. The United Nations estimates that 300-500 million tons of heavy metals, solvents and other waste are released into the world's water supplies each year as a harmful by-product of industrial activity [1]. Water contamination can also be naturally derived. For example, arsenic contamination is a serious issue in countries

such as Bangladesh, West Bengal (India) and Nepal due to the weathering of rocks that naturally contain arsenic [2–6]. Furthermore, as global populations continue to grow the human pressure exerted on our water supplies is expected to intensify with potentially greater likelihood of pollution.

Over the past decade nano-technology has been increasingly investigated as a potential replacement for traditional treatment methods and reactive agents in order to deliver clean water at a reduced cost whilst simultaneously meeting increasingly stringent water quality standards [7]. However, the exact definitions of 'nano-scale' and 'nano-material' are still subjects of controversy. In 2010, the Joint Research Centre (JCR) of the European Commission published a report highlighting the international range of definitions [8]. Just within the UK two definitions were found for the term nano-scale; the UK Department for Environment, Food and Rural Affairs (DEFRA) defined it as ≤200nm, whilst other organizations used ≤100nm. Following recommendations made by the JCR, in October 2011 the European Commission adopted the following definition of 'nano-material' for regulatory purposes [9];

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions are in the size range 1nm - 100nm.

Due to their miniscule size, nano-materials exhibit different physical, chemical and biological characteristics when compared to their larger, micro- and macro-scale counterparts (<100nm) [8;10–13]. The nano-materials have a larger surface area to volume ratio and consequently a higher density of surface reaction sites per unit mass. Furthermore, surface free-energy is observed to be greater than for the corresponding micro- or macro-scale material. Nano-materials, therefore, display a higher reactivity for surface mediated processes. However, as the particle size approaches the electron mean-free path and wavelength scales (below approximately 30nm), quantum size effects become apparent and fundamental physical characteristics are significantly changed again. These effects can counteract the increased reactivity as demonstrated by Sharma et al. [14], with many further comprehensive studies of properties specific to nano-materials readily found in literature.

As just one aspect of the global nano-revolution, the potential use of engineered nano-materials for the treatment of polluted waters has sparked a great deal of interest. Compared to conventional macro-scale sorbent materials (activated carbon, ion exchange resins, manganese oxides, metallic iron, oyster shells, zeolite, etc.), highly reactive nano-materials can achieve the same objective with a reduced mass, theoretically allowing both raw materials and energy to be conserved [7] with significant associated cost savings. Additionally (and significantly) their colloidal size allows subsurface deployment via injection with the rapid treatment of aqueous contaminant plumes at almost any location and depth in terrestrial groundwater systems (Fig. 1).

Conceptually the key properties required for the use of any engineered nano-particle (NP) for in-situ remediation of polluted groundwater are (i) high reactivity for contaminant removal, (ii) high mobility within porous media, (iii) reactive longevity, and, (iv) low toxicity. These properties are operational drivers but at the same time the material must be manufactured and deployed at a cost that is competitive with other existing technologies. Not many engineered NPs fulfil the above mentioned requirements. For example, silver NPss

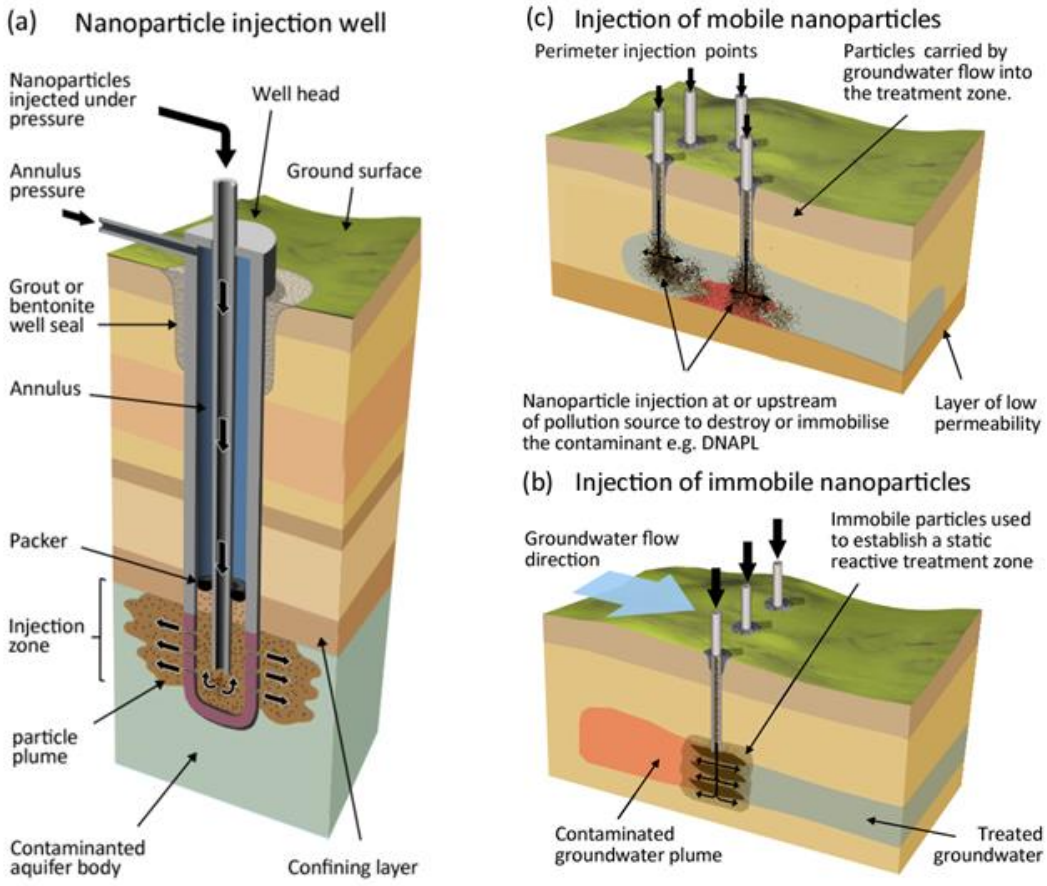

Figure 1: A schematic diagram illustrating the nano-particle injection process [10]

are well recognised for their reactivity with aqueous contaminants and also their stability as colloidal suspensions [15]. However, for groundwater remediation, the material's expense for kilogram quantities, in addition to the well-recognised environmental toxicity issues, precludes their use [16]. Due to its cheap cost, environmental compatibility and high reactivity, the most widely studied nano-material for water treatment is zero-valent iron nano-particles (hereafter referred to as INPs) [17].

From the outset it should be understood that these particles are far from being purely metallic, as an oxide shell is ubiquitous and provies the initial surface via which fluid/contaminant interactions occur. Whilst the following chapter details the development of INP technologies, by association magnetite (Fe_3O_4) NPs are also included as a typically less reactive alternative.

2 Why iron?

2.1 The aqueous corrosion of iron

From a simple perspective, corrosion is the degradation of a material caused by the environment in which it resides. The manufacture of all metals from oxide requires an input of energy and as a result the material has a strong thermodynamic driving force to return to its native low-energy state. This process of reversion is most commonly referred to as corrosion; an inevitable process but one which may be controlled using various

methods. Metallic iron (Fe^0), also referred to as zero-valent iron, is well recognised as being highly susceptible to corrosion in aqueous media. Its corrosion is considered to occur primarily through an electrochemical process, with anodic and cathodic components. The anodic reaction involves the dissolution of Fe^0 (forming soluble ionic products or insoluble oxide/hydroxide) and is coupled with reduction of redox amenable species at the cathode. In natural waters, the primary components available for corrosion reactions are dissolved oxygen (DO) and water, with the former being thermodynamically favoured (Eqn. 1 and 2).

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \longrightarrow 2Fe^{2+} + 2H_2O_{(l)} \qquad E^0 = +1.67V \tag{1}$$

$$2Fe^0_{(s)} + 2H_2O_{(l)} \longrightarrow 2Fe^{2+} + H_{2(g)} + 2OH^-_{(aq)} \qquad E^0 = -0.39V \tag{2}$$

Ferrous iron (Fe^{2+}) is a primary product from these reactions and, in turn, can undergo further oxidative transformation (Eqn. 3 and 4).

$$2Fe^{2+}_{(s)} + 2H^+_{(g)} + \frac{1}{2}O_{2(aq)} \longrightarrow 2Fe^{3+} + H_2O_{(l)} \qquad E^0 = +0.46V \tag{3}$$

$$2Fe^{2+}_{(s)} + 2H_2O_{(l)} \longrightarrow 2Fe^{3+} + H_{2(g)} + 2OH^-_{(aq)} \qquad E^0 = -1.60V \tag{4}$$

Implicit in the above reactions is an increase of solution pH as either protons are consumed or hydroxyl ions are produced. This is commonly observed during the early stages of laboratory-scale INP aqueous reaction experiments. Similarly, due to the high reactive surface area of INPs (up to 100 $m^2\ g^{-1}$), when a significant mass of material is added to an aqueous system, chemically reducing con-ditions can be very rapidly achieved through the production of H_2 (Eqn. 2 and 4); inducing local conditions far from equilibrium and favourable for contaminant removal.

2.2 Environmental reactivity: metallic iron or iron oxide?

During aqueous corrosion both Fe^0 and Fe^{2+} are an active source of $Fe^{3+}{}_{(aq)}$, H_2 and various precipitates such as $Fe(OH)_2$, $Fe(OH)_3$, Fe_3O_4, Fe_2O_3, FeOOH, $Fe_5HO_8 \bullet 4H_2O$ and green rusts. It is these corrosion reactions and the product(s) thereof which are responsible for the reductive transformation and/or physical removal (sorption or enmeshment) of exposed chemical species. As surface precipitated iron oxide/hydroxide is initially porous, the material can develop a 'core-shell' structure during the early stages of reaction with both sorption (at the oxide/hydroxide) and chemical reduction (at the metallic iron oxide/hydroxide interface) able to occur simultaneously. However, as the reaction progresses, increasing quantities of corrosion product(s) and a commensurate lowering in the material's porosity can significantly limit direct Fe^0-H_2O/O_2 and Fe^0-contaminant interactions[18]. It should also be noted at this stage that because the kinetics of the initial stages of Fe^0 oxidation are so rapid, corrosion will proceed even in extremely controlled conditions. Consequently, Fe^0

that is introduced to an environmental system (whether as granular or INPs) will already have a film of surface oxide acquired directly after synthesis. Therefore, from the outset, it should be understood that although this nano-material is referred to as being metallic, each particle exists in natural conditions with a thin but encapsulating layer of surface oxide[19;20].

3 INPs: a versatile material for water treatment

Building on original work by Glavee et al.[21], INPs were first tested for contaminated water treatment by Wang and Zhang at Lehigh University, USA,[22]. Since then INPs have been proven as highly effective for the removal/degradation of a wide range of chemical pollutants, including: β-lactam and nitroimidazole-based antibiotics[23;24]; azo dyes[25;26]; chlorinated solvents[22;27–29]; chlorinated pesticides[30–33]; organophosphates[34]; nitroamines[35]; nitroaromatics[28;36;37]; p-chlorophenol[38]; polybrominated diphenyl ethers[39;40]; polychlorinated biphenyls[22;41]; inorganic anions, including nitrate[42;43], and perchlorate[44]; alkaline earth metals, including barium[45], and beryllium[46]; transition metals, including chromium[46–49], cobalt[50], copper[46;49;51;52], lead[48;52], molybdenum[49], nickel[46;52], silver[52], technetium[53] and vanadium[46]; post-transition metals, including zinc[46;52] and cadmium[46;52]; metalloids, including arsenic[3;4;46;54;55], selenium[56]; and actinides, including uranium[19;46;48;57–59] and plutonium[60]. Due to the significant variation in contaminant chemistry, numerous possible contaminant removal pathways have been determined, including sorption, complexation, (co)precipitation and surface mediated chemical reduction (Table 1)[61].

Table 1: Calculated cell potential (E^0 Cell (V)) using the Nernst equation for iron-contaminant metal systems, where Fe^0 is considered the anode material. E^{mx1} Cell (V) and E^{mx2} Cell (V) represent excess $Fe^{2+}{}_{(aq)}$ with respect to the other aqueous metal at molar ratios of 100:1 and 10,000:1 respectively.

Redox couple	**E^0**	**E^{mx1} Cell (V)**	**E^{mx2} Cell (V)**	**Predominant removal mechanism using Fe^0**	Eq.
$Zn^{2+} + Fe^0 \longrightarrow Zn^0 + Fe^{2+}$	-0.35	-0.29	-0.23	Sorption/surface complexation	(5)
$Cd^{2+} + Fe^0 \longrightarrow Cd^0 + Fe^{2+}$	0.01	0.07	0.13	Sorption/surface complexation	(6)
$Pb^{2+} + Fe^0 \longrightarrow Pb^0 + Fe^{2+}$	0.28	0.34	0.39	Sorption with partial chemical reduction	(7)
$Ni^{2+} + Fe^0 \longrightarrow Ni^0 + Fe^{2+}$	0.17	0.23	0.29	Sorption with partial chemical reduction	(8)
$Hg^{2+} + Fe^0 \longrightarrow Hg^0 + Fe^{2+}$	0.68	0.74	0.80	Reductive precipitation	(9)
$Cu^{2+} + Fe^0 \longrightarrow Cu^0 + Fe^{2+}$	0.78	0.81	0.87	Reductive precipitation	(10)

As suggested by Li and Zhang[52], for metal ions such as Cd^{2+} and Zn^{2+} which have standard electrode potentials (E^0) for reduction to a metallic state that are very close to, or more negative than, Fe^0 (-0.41 V), the removal mechanism by INPs occurs predominantly via sorption/surface complexation. In comparison, with metal ions such as Hg^{2+} and Cu^{2+}, which have E^0 much more positive than Fe^0, removal occurs predominantly via surface mediated reductive precipitation. Where metal cations are only slightly more electropositive than iron, such as Ni^{2+} and Pb^{2+}, sorption, with partial chemical reduction, has been shown to occur. It is recognised, however, that aqueous INP treatment systems do not exist at standard conditions and consequently the above comparison of potentials is questionable. Instead the Nernst equation may be used to relate standard cell potentials to those actually existing. As displayed in Table 1, the presence of a significant molar excess of aqueous Fe^{2+} derived from the rapid anodic dissolution of the INPs can significantly alter the cell potential from the standard value (due to alteration of the thermodynamic reaction quotient), making contaminant reduction reactions more favourable.

The most recognised mechanism by which Fe^0 and Fe^{2+} solid materials remove contaminants from groundwater is via chemical reduction, and typically requires the contaminant to be adsorbed or in close proximity (electronic range) to the iron surface. For the treatment of organic contaminants, such as chlorinated organics and polychlorinated biphenyls, removal generally occurs via the reductive degradation of the chemical, i.e. the contaminant is physically destroyed. In contrast, for the treatment of many heavy metals and radionuclides removal typically occurs via immobilisation. Contaminants are merely removed from the water and trapped in an immobile state without physical destruction. For in situ remediation of heavy metals and radionuclides it is therefore significant to note that, as recovery of the injected nano-materials (with associated contaminants) is unfeasible, contaminants are neither destroyed nor extracted from the system. This presents the prospect for future contaminant remobilisation should geochemical conditions change. Considering the significant geochemical perturbation caused by INP injection, subsurface treatment zones are often highly metastable, and even a gradual reversion in groundwater conditions toward a pre-injection state may be enough for significant remobilisation to occur. This is a key issue which may limit the development of the technology and is discussed in Section 3.3.

3.1 INP synthesis

To date, numerous methods have been developed for the manufacture of metallic NPs, including chemical vapour deposition, inert gas condensation, pulsed laser ablation, spark discharge generation, sputtering gas-aggregation, thermal decomposition, thermal reduction of oxide compounds, hydrogenation of metallic complexes and the aqueous reduction of iron salts. These manufacturing methods can be considered as either 'bottom up' or 'top down' approaches. The former involves physical or chemical methods to construct a nano-material from basic building blocks, such as atoms or molecules. The latter involves physical or chemical methods to breakdown or restructure a bulk material to the nano-scale. Fig. 2 highlights the differences in particle morphology obtained by different manufacturing routes.

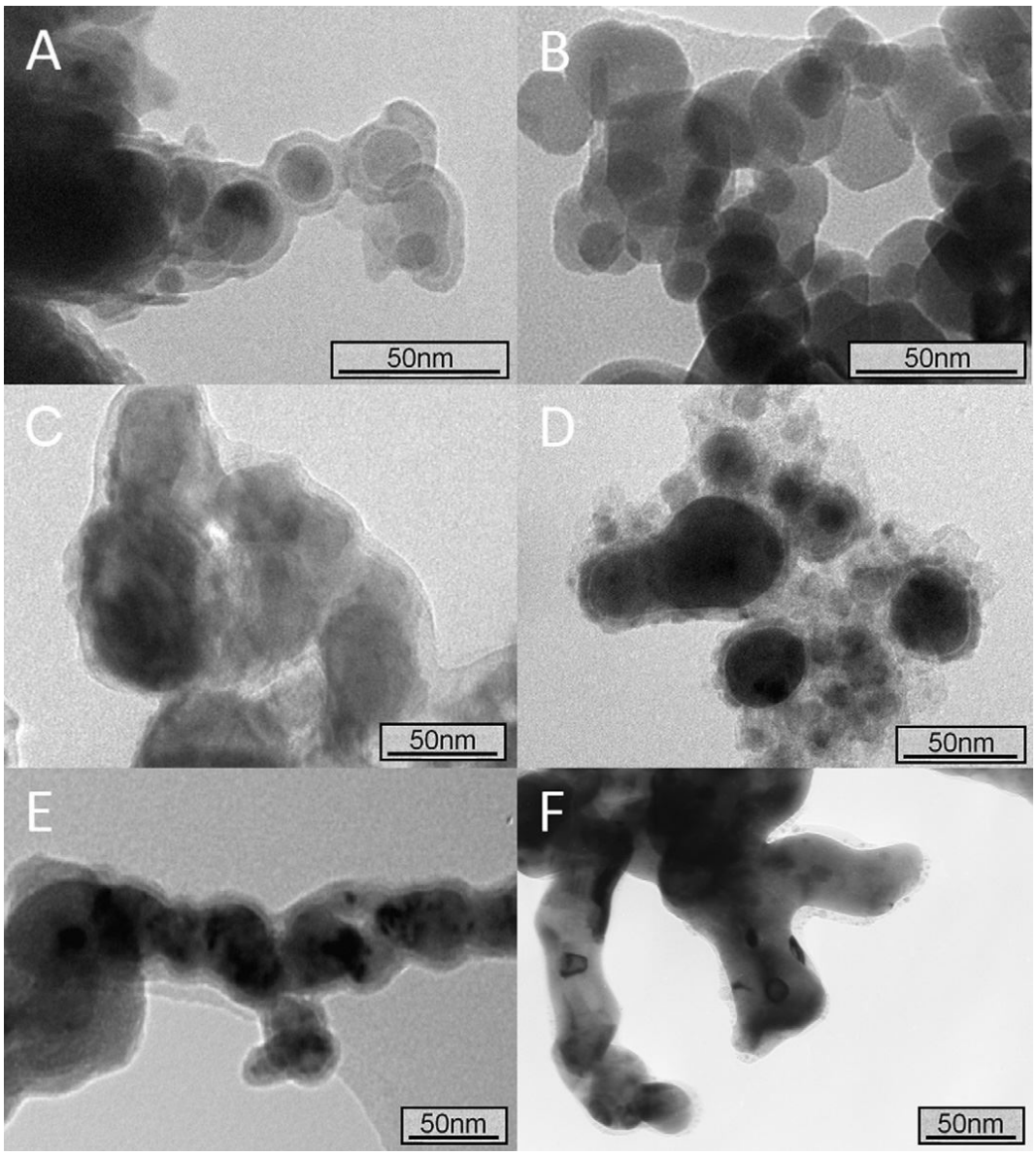

Figure 2: Transmission electron microscopy (TEM) images of different iron nanoparticles manufactured or purchased by the authors for this review. (A) nZVI synthesised by the reduction of aqueous Fe^{2+} using sodium borohydride[22]; (B) nanoscale magnetite, purchased from Sigma-Aldrich (PubChem Substance ID: 24882829)[19]; (C) NANOFER STAR, purchased from NANO IRON, s.r.o.[62]; (D) nZVI synthesised by the carbothermal reduction of aqueous Fe^{2+}[63]; (E) nZVI synthesised by the reduction of aqueous Fe^{2+} using green tea polyphenols[64]; and (F) nZVI synthesised by the reduction of aqueous Fe^{2+} using sodium borohydride then annealed under vacuum (at least 10-6 mbar) at 500 °C for 24 h[20]

With the manufacture of gram-quantity INPs achieved using simple chemical reagents and minimal specialist lab equipment, the borohydride reduction of ferrous salts is the most widely studied method within academia (Fig. 2A)[22]. The method produces highly reactive INPs; however, the NPs are often highly polydispersed, ranging over tens to hundreds of nano-metres in size and thus significantly prone to agglomeration[13;20;65]. Expensive reagents and the production of large volumes of hydrogen gas also preclude its industrial application[63].

3.1.1 The thermal reduction of ferrous iron

The carbothermal reduction of ferrous iron has recently been investigated as a potential method for the manufacture of cheap and functional INPs (Fig. 2D). Analogous to the production of iron and steel from ore, the

method regards the use of thermal energy and gaseous reducing agents (H_2, CO_2, CO, etc.) produced during the thermal decomposition of carbon-based materials (carbon black, carbon NPs, hollow carbon, ultra-fine graphite powder, etc.) to drive the reduction of IONPs[66] or aqueous Fe^{2+} [63]. With high surface area carbon is an extremely cheap and readily available material (e.g. carbon black is a waste product from the fossil fuel industry), both methods represent cheap routes for the manufacture of various different INP physicochemical forms. Additional to this, despite the high temperatures (>500 °C) required for the formation of Fe^0 in preference to its oxides, the reaction is endothermic, with only gaseous by-products, and therefore represents a scalable process.

3.1.2 Electrolysis

As a well-established industrial method for the sequestration of metals from ionic solution, electrolysis has recently been investigated for INP synthesis. Requiring only: Fe^{2+} salt solution, a conductive substrate, a direct current and a method to disperse electro-deposited NPs, the method represents an extremely simple, cheap and quick method for the production of INPs. The only issue is determining appropriate methods for the dispersion of newly formed metallic NPs at the cathode. Recent attempts include Chen et al. using ultrasonication[67], and Wang et al., 2008 using ion-exchange in a nafion film[68], represent highly promising methods.

3.1.3 Polyphenolic plant extracts

Perhaps the most environmentally compatible process developed so far for the synthesis of INPs is the reduction of Fe^{2+} using polyphenolic plant extracts (Fig. 2 E). This method, developed by scientists at VeruTEK and the US EPA involves the preparation of a polyphenolic solution by heating specific plant extracts (coffee, green tea, lemon balm, sorghum bran, etc.) in water to near-boiling temperature, extracting the supernatant and mixing it with a Fe^{2+} solution[64]. The method has also been shown as possible at ambient temperature, allowing the potential for INP synthesis in situ and eliminating the need for offsite manufacture, storage and transport. Primarily developed as an in situ soil catalyst to improve the performance of in situ chemical oxidation, the process is yet to be tailored to synthesise INPs that can be used for water treatment as a chemical reducing agent.

3.2 How much do INPs cost?

Although iron is inexpensive in bulk form, reactive NPs are much more expensive because of the materials and processes needed to make them. Additional to this, site remediation is an unwanted (and often unplanned) financial burden and as such environmental technologies typically exhibit a relatively low market value[69]. In 2004 the price for INPs varied between £15 and £100 per kg, whilst micro and granular Fe^0 were available for less than £1 per kg[70]. Depending on the type and amount ordered INPs today costs in the range of £50-150 per kg. In order to compete against existing water treatment methods, such as in situ chemical oxidation, the

price of INPs must reduce to approximately <£10 per kg[71]. Consequently, in recent years there has been much investigation into the development of methods to produce cheap multi-kilogram quantities of INPs, whilst maintaining reactivity and/or functionality.

In 2006, Toda Kogyo Ltd. developed a method that uses hydrogen as a reducing agent for IONPs at 350-600 °C[72]. Although the process is scalable and has reached commercial status it involves a number of chemical processing steps to synthesise the IONPs and then reduce them in a batch process. In recent years, the market leader for large-scale field deployment of INPs has arguably been Golder Associates Inc., who produce INPs in large quantities by the mechanical attrition of macroscale Fe^0 in planetary ball mill systems[73]. Whilst it is a straightforward method, it is highly energy intensive; and newly formed particles exhibit a very high surface energy and are thus prone to aggregation.

3.3 Are INPs as good as some studies suggest?

With INPs proven as highly effective for the removal of a wide range of contaminant species from simple synthetic solutions, subsequent work has focussed on determining the materials' performance for the treatment of chemically complex and/or "real" solutions. It has been outlined that some previous studies using 'simple solution' tests, lacking complexing agents and/or competitive chemical reactions, have largely overestimated INP performance[19;57;59;74]. This is also evidenced by the limited number of field studies that have reported poorer than expected INP performance, with an unexpected need to provide multiple treatments to attain successful clean-up[75;76].

This behaviour was clearly demonstrated in a recent study[19], where INPs were tested for the removal of uranium (U) from groundwater samples containing high concentrations of dissolved bicarbonate, in comparison to a laboratory synthetic water system. The INPs were observed as highly effective for the rapid removal of U from the groundwater despite their complex chemistry and provided a comparable performance to the simple U-only water system. However, over extended time periods (>1 week) near-total re-release of U was recorded from the groundwater system, which was not observed in the simple U-only system over the entire three month treatment period, Fig. 3.

The mechanism was attributed to incomplete chemical reduction of surface-precipitated U (from soluble U(VI) to insoluble U(IV) within the groundwater samples, allowing the re-release of U(VI) during NP corrosion[19;77;78] and the reformation of highly stable (nominally carbonate) aqueous U-complexes. Taking uranium as an example, Table 2 shows the significantly enhanced aqueous stability of U^{6+} in the presence of certain complexing agents which are common in natural waters.

A typical groundwater in the vadose zone has a CO_2 pressure of 10^{-2} bar which is elevated with respect to rivers and other surface waters (10-3.8 bar)[81]. For uranium, the presence of CO_2 and also bicarbonate (HCO^{3-}) in water promotes the formation of uranyl-carbonate complexes UO_2CO_3 (pH 3-5), $UO_2(CO_3)_2{}^{2-}$ (pH 5-8) and $UO_2(CO_3)_3^{4-}$ (pH>8) in favour of uranyl-hydrate complexes, which have lower thermodynamic stability. This is recognised to have a profound effect on the adsorption behaviour and commensurate mobility

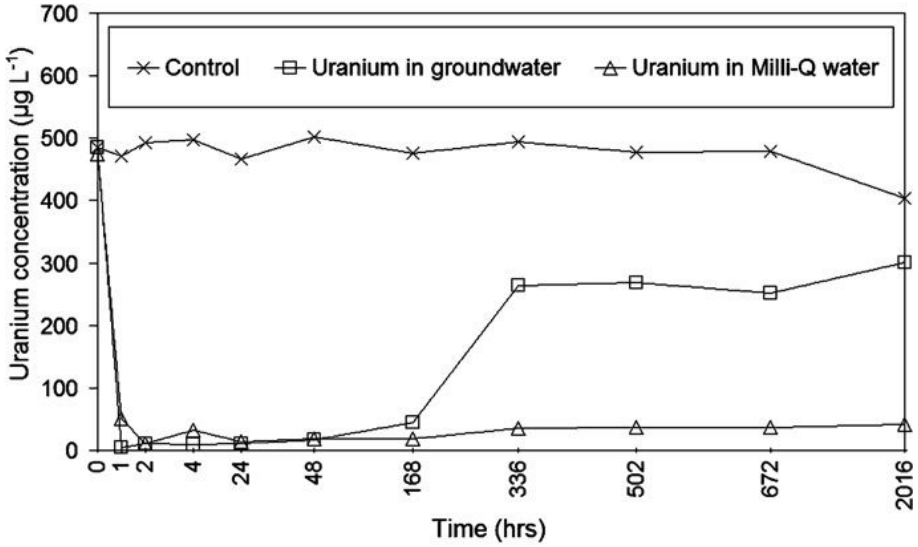

Figure 3: The removal of aqueous uranium from groundwater and Mill-Q water using nZVI at 0.25gL^{-1} over a 3 month time period[19].

Table 2: Stability constants of aqueous U^{6+} in the presence and absence of certain complexing agents found in environmental waters[79;80]

Association reaction	**Log$K$**	**Eq.**
$U_2^{2+} + CO_3^{2-} = UO_2CO_3$	9.68	(11)
$U_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.94	(12)
$U_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.60	(13)
$U_2^{2+} + PO_4^{3-} = UO_2PO_4^-$	13.23	(14)
$U_2^{2+} + SO_4^{2-} = UO_2SO_4$	3.15	(15)
$U_2^{2+} + H_2O = UO_2OH^+ + H^+$	-5.2	(16)
$U_2^{2+} + 2H_2O = UO_2(OH)_2 + 2H^+$	-12.0	(17)
$U_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	-5.2	(18)

of dissolved uranium in its hexavalent state and thus its affinity for remediation[19;77;78].

As studies to date have largely overlooked the influence of complexing agents ubiquitous in natural waters, more empirical tests are required to characterise the extent at which other heavy metals and radionuclides will display the same remobilisation trend. An obvious mitigation strategy in field applications would be either: (i) to deploy a mass of INPs significantly in excess of that required; or (ii) to resupply the contaminated zone with INPs on a regular basis. Both strategies have been reported in field trials as ways to improve efficacy, but perhaps have not been fully understood from a geochemical perspective. There accordingly exists a fundamental future need to examine the reversible nature of remediation in complex and/or natural waters using INPs. This will provide validation of the technology for sites where assurance of medium to long-term immobilisation of contaminant heavy metal and radionuclides is required.

4 Operational drivers for water treatment

The structure, geochemistry and hydrogeology of each polluted site is unique and INP injection highlights multiple disadvantages of using 'free' NPs for remediation including the important fact that NP behaviour is still not fully understood. Resultantly the strategy adopted for INP deployment must take into account various

operational parameters. Variables that may be altered to optimise INPs performance include the particle size range (Section 4.1), mobility (Section 4.2), reactivity and longevity (Sections 4.3 and 4.4), injection strategy (Section 4.5) and the material's ecotoxicity (Section 4.6).

4.1 INP size

It is logical to suggest that by providing the highest surface area for reaction, the very smallest INPs would provide the best performance for contaminant removal. However, there exists the possibility that at this size range (<20 nm) the resultant particles are too reactive to be useful for in situ environmental applications, with reactive exhaustion likely to be achieved in a very short time. Indeed, for achieving optimal INP performance at any given site, it should be acknowledged that there is a conceptual play-off between the reactivity and longevity of the material. Particles of sufficient size must be selected to guarantee in situ reactivity and avoid reactive exhaustion during storage, transit and subsurface deployment.

When considering the reactive capacity of INPs, an additional factor to acknowledge is the proportion of the particle which is oxide compared to Fe^0, as a function of particle size. Assuming an oxide thickness independent of nano-particulate size, in some circumstances it may account for significantly more of the volumetric fraction than Fe^0. For example, a spherical INP of 25 nm total diameter with a surface oxide 3 nm thick would be 56% oxide by volume, Fig. 4. Consequently, in typical conditions the smaller the particle the higher the volume of constituent oxide, implying that at very small nano-size (<10 nm) Fe^0 may only represent a small fraction of total nano-particulate volume.

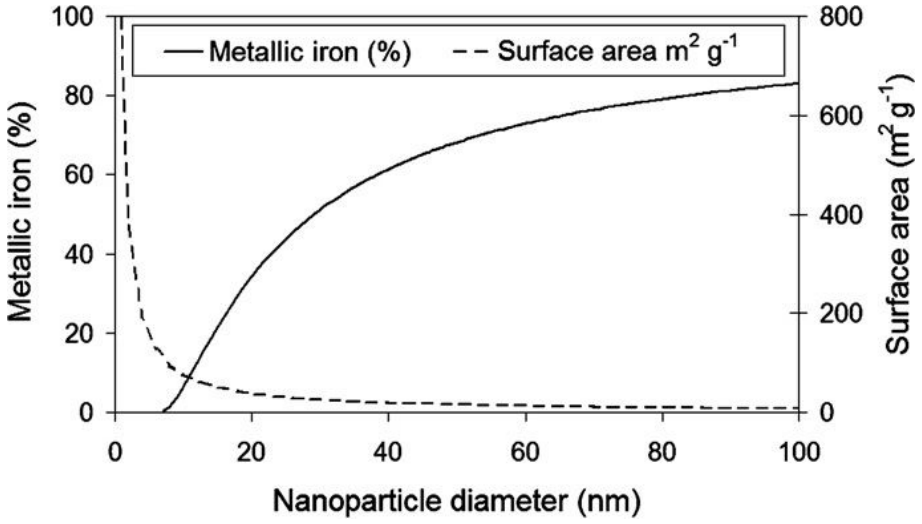

Figure 4: Metallic iron content (%) and surface area (m^2g^{-1}) calculated as a function of NP diameter. Both variables are calculated for perfectly spherical NPs and are therefore not intended to directly represent empirical data. Metallic iron (%) assumes a surface oxide thickness of 3 nm, independent of nano-particle diameter. Surface area (m^2g^{-1}) assumes perfectly dispersed nano-particles, and therefore does not include changes in surface area due to nano-particulate agglomeration/aggregation [10].

4.2 Improving mobility

There is abundant evidence and now a broad consensus that the mobility of INPs in porous media is very limited under almost all conditions; see [82] and references therein. Without the application of surface coatings to aid colloidal stability, rapid aqueous aggregation of standard INPs is frequently observed due strong magnetic properties [82–86] and electrostatic NP-NP attractions, which operate most effectively in concentrated particle suspensions (i.e. slurries). Indeed, early pilot scale field trials have indicated extremely poor INP subsurface migration, with maximum practical transport distances of only a few metres reported for bare unsupported particles in saturated sediments [82]. Particle aggregation and pore clogging were determined as the causal mechanism, with the very limited mobility of INPs explained by three primary mechanisms: (i) particle aggregation and subsequent gelation caused by poor colloidal stability; (ii) the formation of voluminous corrosion product precipitates from particle oxidation/corrosion; and (iii) particle removal from solution by interaction with subsurface components, e.g. attachment to mineral surfaces and carbonaceous materials or via microbial removal. See [82;87–89], and references therein for a more comprehensive review.

An illustrative example of rapid aqueous aggregation is evidenced in Fig. 5 which displays a backscattered electron microscopy image taken of unmodified INPs in Milli-Q water buffered at pH 7. The image was taken using a Quanto-mix capsule to hold the fluid suspension.

In groundwaters, it is certain that the interaction of injected INPs with mineral surfaces will be continual. Particle collisions with these immobile subsurface components are estimated to occur in the order of hundreds per metre travelled [90]. Thus, for particles to be effectively transported nearly all of these collisions must be unsuccessful, i.e. the "sticking probability" must be very low. Consequently, the key to improving particle mobility is found in modifying their surface properties such that the INPs have significantly improved colloidal stability and an associated reduction in the likelihood of adherence to mineral surfaces. Fig. 6 demonstrates different modification techniques. Yet the challenge with any INP modification is to simultaneously maintain the material's reactive performance. An alternative method to improve the material's mobility without changing its surface properties is to increase the particle size. The consensus within the industry is that, depending on the permeability of the soil, particles within the size range of 0.1-2μm have the highest mobility [71]. An additional advantage of using such particle size fractions is that any nano eco-toxicological issues are precluded. Additional to this, larger particle size fractions (>0.5μm) can be handled as powder (rather than as slurry), reducing the material's volume and thus improving material handling. Large-scale field tests are planned at the VEGAS research facility to investigate this [71]. Accompanying this, fundamental investigations into the extent at which an increase in particle size affects the material's reactivity, functionality and contaminant removal efficacy are required.

4.2.1 Surfactants

It is well accepted that particle mobility may be improved through the use of surfactant [10;41;55;89;91–95] and other polymer coatings [35;47;74;82;88;96–121]. Work first carried out in the 1960s based on ferrofluids applicable

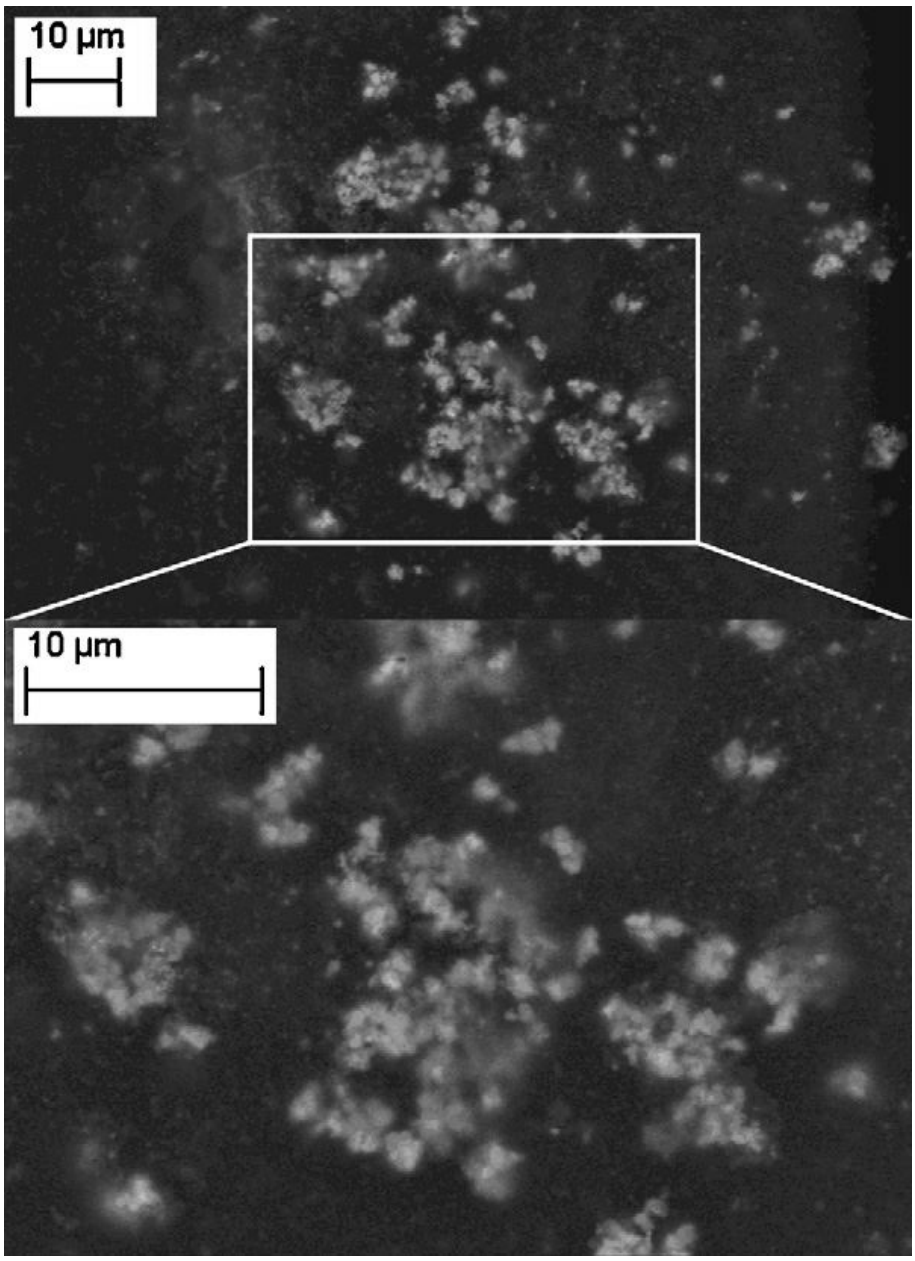

Figure 5: A backscattered electron microscopy image of unmodified INPs in Milli-Q water buffered to pH 7. [10].

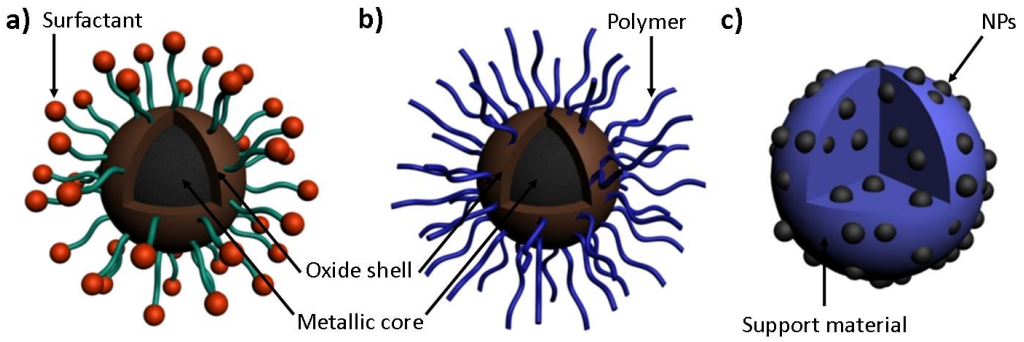

Figure 6: Schematic of the different modifications that can be made to improve mobility of INPs; a) Surfactants, b) polymers and c) support.

for magnetics, optics, biophysics, medicine, rheology and even thermodynamics has since provided the basis for current INP coating technologies. Ferrofluids are classified as stabilised colloidal mixtures of magnetic NPs suspended in a carrier fluid that become strongly polarised in the presence of a magnetic field. Particle stabilisation is achieved through the use of surfactants, polymeric surface coatings and chemicals to control the surface particle charge.

Applied to INPs, the steric hindrances provided by such coating molecules counteract the electrical and dipolar attractions between particles and promote colloidal stability. This is only achieved when a sufficient mass of coating material or surfactant is present to form a complete micelle. Resultantly, the use of surfactants in INP injection technology has limited environmental applicability because, following injection, particle dispersion will be commensurate with rapid desorption of the surfactant into the groundwater, effectively losing any previously imbued particle stability.

4.2.2 Polyelectrolyte coatings

As an alternative to surfactants, the controlled coating of INPs with high molecular weight polymers may be considered an irreversible process and therefore provides a more appropriate method for increasing the hydraulic mobility of INPs in subsurface systems. Working in the same way as surfactants to promote colloidal stability (steric hindrances) the polymer is physically or chemically grafted to the NP surface [122]. An additional benefit is that the polymer coatings may also act as an energy source to stimulate microbial activity, which may aid contaminant removal particularly in carbon limited environments [123].

Numerous polyelectrolyte (polymer) coatings have been tested with varying success, including butyl methacrylate [124], caboxymethyl cellulose [74] and [109], guar gum [111], poly(4-styrenesulphonate) [125], polyacrylic acid [82], polyaspartate [109;126], polyoxyethylene sorbitan monolaurate [55], poly-methylmethacrylate [124], polymethacrylic acid [124], polystyrene sulphonate [109], polyvinyl alcohol-co-vinyl acetate-co-itaconic [94], triblock copolymers [127], and xanthan gum [97]. Over a broad range of groundwater conditions these types of coatings are observed to persist for periods of several months [123].

Two commonly studied materials are carboxymethyl cellulose and guar gum. Formed from cellulose and guar beans respectively, both polysaccharides are extremely cheap, non-toxic, naturally water-soluble and biodegradable. In water, both species are non-ionic and hydrocolloidal, remaining neutrally charged and unaffected by ionic strength or pH across an environmentally relevant range (pH 5-9) [74;111]. It seems likely that other approaches for improving colloidal stability of INPs will arise in the future based upon exploiting the plethora of cheaply available biopolymers, improving on production cost, functionality and environmental compatibility. Biopolymers such as alginate and potato starch have already been examined and proven as unsuccessful [111], but other more successful candidates may well arise in the near future.

4.2.3 Improving the mobility of INPs for the remediation of non-aqueous phase liquids

Researchers at the Kennedy Space Center (NASA) and the University of Central Florida have recently developed a new method for the treatment of non-aqueous phase liquids (NAPL) called “emulsified nano zero valent iron”

(E-nZVI)[128]. It is one of only a few methods invented which can be used for effective in situ treatment of a dense non-aqueous phase liquid (DNAPL) plume. E-nZVI is comprised of an agglomerate of INPs particles packed into a droplet surrounded by surfactant and oil layer which forms an oil-liquid membrane. The hydrophobic membrane allows the DNAPL to diffuse through, whereupon it undergoes reductive dechlorination by the E-nZVI in the aqueous phase. The protective membrane also allows the E-nZVI to: move through the subsurface as a DNAPL, therefore improving its chances for DNAPL exposure; and operate in sites of high dissolved oxygen and/or salinity, with iron particles inside the membrane protected from corrosion. Encapsulating the INPs in a hydrophobic membrane also protects the material from reactions with unwanted groundwater constituents such as inorganics that might otherwise act to decrease its reactive capacity. Additional methods include the use of triblock copolymers[127], and a range of surfactants and biodegradable non-polar oils[129–132].

4.2.4 Protective shells and solid supports

The use of protective shells, originally designed for magnetic applications including data storage[133;134], drug-delivery[135], medical imaging[136] and protein purification[137], has also received interest with regard to improving the hydraulic mobility and longevity of INPs. Coatings tested include silica[138], polymers[139] and carbon[63;140], and have been observed to improve INP stability to a level comparable with polyelectrolyte coatings. Due to its high stability in acidic or basic media and proven biocompatibility, the use of carbon has typically been preferred.

The use of solid supports has also been tested. A method developed by scientists at the Helmholtz Centre for Environmental Research in Germany[141] has combined INPs with activated carbon to produce "Carbo-Iron" platelets of between 50 and 200 nm diameter. The combined NAPL sorbent properties of the activated carbon with the reductive capacity of the Fe^0 has proven very promising for the reduction of a range of chlorinated organics whilst also exhibiting hydraulic mobility comparable to surfactants and polyelectrolyte coatings.

4.3 Improving reactivity; bimetallic NPs

A well-documented method for increasing the chemical reactivity of INPs has been to alloy it with a nobler metal (Pd, Pt, Ag, Ni, Cu, etc.). In recent years numerous experimental studies of bimetallic INPs for contaminant remediation have been made, including Fe/Pd[27;76;142–144], Fe/Pt[142], Fe/Ag[145] and Fe/Ni[142;146–149]. In such electrochemical couples, Fe^0 is considered to behave as an anode, becoming sacrificially oxidised to galvanically protect the noble metal. Experiments have yielded varying results for particle performance, with Fe-Pd generally out-performing the other combinations. Chemical reduction of sorbed contaminants at the bimetallic INP surface is considered to occur through either direct electron transfer with the noble metal or through reaction with hydrogen produced by oxidation of Fe0. Hydrogen is likely present as a dissolved gas, some of which is adsorbed to the particle surfaces, with an undetermined fraction possibly present as active metal hydride having undergone diatomic dissociation and reaction with the exposed noble metal[142].

For the clean-up of chlorinated organic contaminants such as TCE or PCP, hydrogen is observed to be

the predominant driver for degradation, by breaking C-Cl bonds and swapping itself for chlorine, which is liberated as a gas[146]. For bimetallic INPs, an advantageous consequence of the inferred catalysis is that dichloro-ethelyenes (DCE) and vinyl chloride (VC), which are generated by TCE breakdown, are observed to be rapidly hydrogenated at the particle surfaces and do not accumulate in the reaction[146]. By comparison, TCE reduction has been recorded as significantly limited by monometallic INPs[146;149], with the accumulation of DCE and VCs often observed[29;150]. This occurs because direct reduction of water by Fe^0 proceeds more slowly without a galvanic influence and resultantly the hydrogenolysis of the contaminant specie is limited.

4.3.1 Will bimetallics prevail over monometallics?

In the US, approximately 40% of all INPs remediation projects use bimetallic INPs (approximately 50% use standard INPs) whilst in Europe no field application using bimetallic particles is yet to take place[71]. For the commercial deployment of bimetallic INPs, two unavoidable facts are that: (i) they will only be adopted in preference to monometallic INPs if they offer significantly improved performance at a competitive price (high value metals such as Pt, Pd and Ag are likely to prove too costly); and (ii) there are still considerable concerns over the ecotoxicity of some of the noble metals chosen for alloying. For example, Ni is considered a hazardous substance by the UK Environment Agency[151].

Within bimetallic INPs systems, efficiency of the cathodic reaction is found to determine the particle corrosion rate. If the rate is high, contaminant reactivity will also be high but reactive longevity will be poor. Consequently, it is suggested that, bimetallic INPs are generally best suited for remediation applications where only short migration times to the contaminant plume are required. It is apparent from the literature that bimetallic INPs reactivity depends on a range of factors, including NP size, physicochemistry, and the choice and quantity (%) of the noble metal. Some studies have documented minimal improvement with respect to their monometallic counterpart,[59] whilst others report an enhancement by several orders of magnitude[147]. There is a resultant need for fundamental characterisation and quantification of the reactivity of different bimetallic INPs materials (Section 6).

4.4 Improving physico-chemical structure: Thermal treatments

Recent attempts to improve the physico-chemical structure of INPs without the use of alloying or dopant materials (and their aforementioned disadvantages) have examined the use of thermal treatments in vacuo.

It is well established that a wide variety of INP synthesis methods, including the most common method, the borohydride reduction of Fe^{2+}, are observed to result in the formation of significant physicochemical imperfections within the forming crystal lattices, within both the bulk metal and the surface oxide layer[20]. This is seen to alter significantly particle reactivity[19;20;57;59;152;153]. As a consequence, thermal treatment (or annealing), a process commonly used in metallurgy to relieve internal stress, refine grain structure and produce equilibrium conditions within a metal has been considered as an appropriate method to improve the physico-chemical composition of INPs[19;20;57;59].

Vacuum annealing of INPs at 500°C at less than 10-5 mbar for 24 h is observed to result in numerous physico-chemical effects on INP structure[20]. Changes include a reduction in surface area by up to 75% (from 19.0 to 4.8 m^2g^{-1}) related to diffusion bonding of previously discrete particles, but, with an accompanying improvement in physical structure and surface chemistry, including: (i) reordering and recrystallisation of the metallic cores; (ii) concurrent thinning, dehydration and stoichiometric refinement of the surface oxide; and (iii) migration of impurities toward the particle surfaces and grain boundaries. A comparative study of annealed and non-annealed INPs for contaminant remediation has since shown that vacuum annealed INPs exhibit similar or improved levels of contaminant removal, but with a marked decrease in Fe dissolution[59]. Taking into account the reduced surface area, annealing was demonstrated to significantly increase particle reactivity and has been ascribed to the formation of an effective electronic network within the annealed INP structures, related to the increase of Fe^{2+} relative to Fe^{3+} in the surface oxide and its refinement into a uniformly structured magnetite (Fe_3O_4) layer around the metal core[59].

Magnetite has an inverse spinel structure that accommodates both Fe^{2+} and Fe^{3+} in octahedral sites and exhibits effective electron hopping between these sites. Consequently magnetite is a strong semiconductor (102-$103\Omega^{-1}cm^{-1}$) and when formed as a film on Fe^0 is likely to provide a catalytic surface site, facilitating electron transfer from the metal to the oxide, as previously reported[154]. In unmodified INPs the surface magnetite is defective, poorly crystalline and may co-exist with other non-conductive oxide phases. Consequently, the catalytic behaviour of the surface oxide is considered to be limited and in the early stages of aqueous activity, where direct electrochemical corrosion and dissolution of the Fe^0 may be observed until a uniform oxide is formed. By comparison, the magnetite present on annealed INPs is determined to be uniform with refined stoichiometry and good electron conductivity such that conductive behaviour is greatly improved and direct contact of the zero valent iron with water (or constituent contaminants) is prevented, Fig. 7.

Resultantly, particle reactivity is improved whilst also limiting initial corrosion rates. Results have also indicated that contaminants such as uranium are retained for longer periods on annealed INPs, perhaps indicating that in the early stages of reaction a greater proportion of the sequestered U^{6+} is converted to U^{4+} oxide via surface catalysed reductive precipitation[89].

4.5 INP injection strategy

With NP injection conceptually possible at almost any location and depth in a terrestrial groundwater system, the method employed, and the distribution and quantity of injection wells, typically depend on the geology and geochemistry of a contaminated site and not on the location of the contaminant plume. This is unless plume depth is great enough to incur project-limiting deployment costs due to requirements for higher injection pressures and/or larger infrastructure. Subsurface inhomogeneities, such as highly consolidated layers, cobblestones, cracks and fissures, and sub-aerial features, such as monoliths, rivers, buildings and roads, may also affect the proposed injection location(s). However, most vendors typically use a relatively aggressive injection method, often involving hydraulic and/or pneumatic fracturing of the medium to facilitate INP movement into

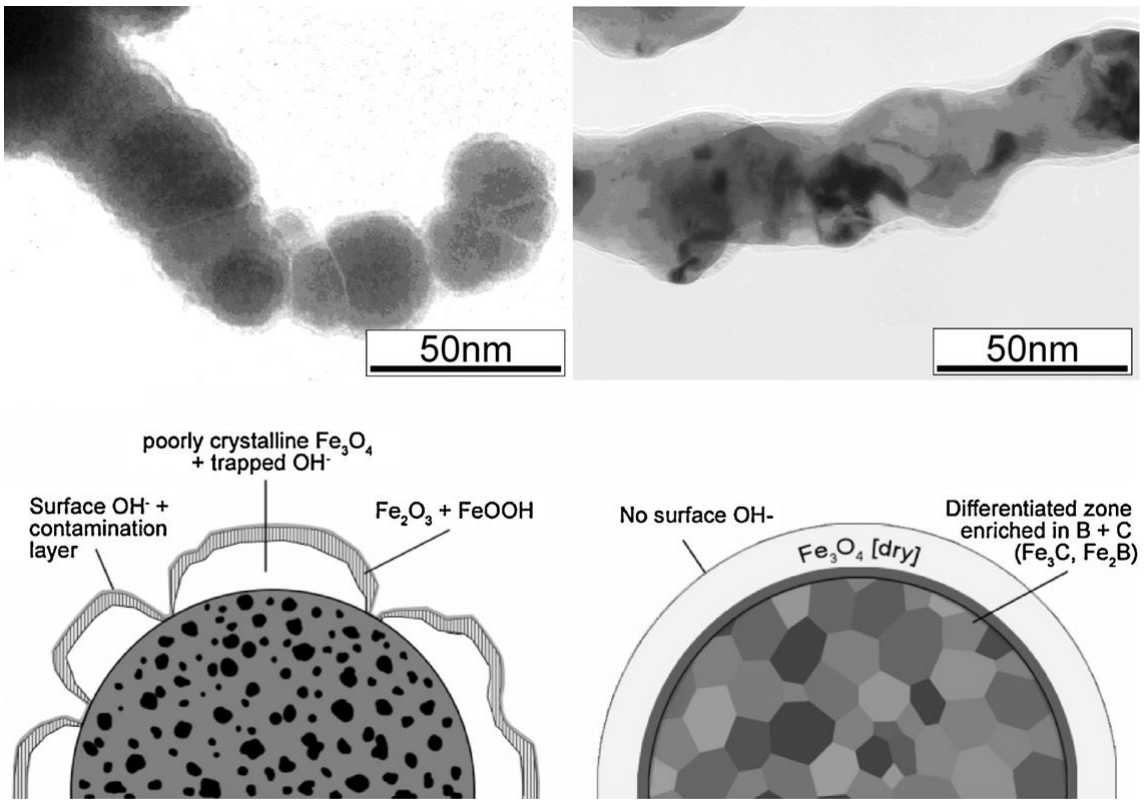

Figure 7: A transmission electron microscope (TEM) image of: as-formed INPs (top left) and; (B) vacuum annealed INPs (top right). An illustration of the perceived structural transformation of: as-formed INPs before (bottom left) and; vacuum annealed INPs (bottom right) [20]

soil pores.

In order to perform an effective site evaluation, all geologic and plume heterogeneities must be determined along with a model of all hydraulic and chemical parameters. Once this has been achieved can the geo-environmental engineer theoretically and/or only determine (using water and sediment samples taken from the site) whether INPs are appropriate, and if so: (i) the approximate INP composition and; (ii) the deployment strategy. A pilot test is then performed in a small area of the site to determine any unforeseen challenges associated with the project. Data and evidence can then be collated to determine a tailored remediation strategy, including: the composition, quantity and concentration of the INP slurry mixture, along with the injection apparatus, location(s), depth, orientation, pressure, flow-rate and duration. Other logistical factors that must be considered include: workforce safety, the potential for accidental INP release, the impact the project may have on local flora and fauna populations and, the strategy for monitoring and any repeated treatments.

As proposed by Tratnyek and Johnson [84], the method of INP injection can be tailored for the treatment of mobile or immobile contamination, Fig. 1.

For the treatment of mobile contaminant plumes, low mobility INPs are typically used for the formation of a “reactive treatment zone” The NPs are sequentially injected and adsorb to native aquifer material, forming a physico-chemical filter. For the treatment of a static contaminant body, namely non-aqueous phase liquids (NAPL), mobile INPs are typically selected and injected upstream for direct treatment. Whilst theoretically

robust from a simplistic perspective, both methods are reliant on extremely accurate control over site conditions and INP corrosion rate. Compared to permeable reactive barrier technologies, very little is known about the effect of pore clogging (size exclusion) caused by the physical presence of INPs and their voluminous corrosion products. For example, ferrihydrite ($Fe_2O_3 \circ H_2O$) is up to 600% larger than an equal mass of Fe^0 [155]. In certain circumstances this could prove beneficial. However, if applied incorrectly, the contaminant plume could be inadvertently directed to a different location. This is an extremely significant factor and has largely been overlooked in the literature [155].

As mentioned in 3.3, the type and concentration of groundwater geochemical constituents (including contaminants) has a strong bearing on the INP deployment mechanism, with a large quantity of INPs typically required for chemically complex waters, and to prevent the remobilisation of heavy metals and radionuclides. Also, the presence of electron donors, especially in aquifer sites that have glacial outwash sediment from bedrock, can cause unwanted INP agglomeration and subsequent gelation and pore clogging. Consequently, in addition to standard site monitoring procedures, a determination of the physical distribution and chemical form of INPs in the subsurface would be highly desirable; to provide direct feedback as to the progression/evolution of the deployment system. At present, there is no field-portable device available that can detect NPs in situ. However, measurement of groundwater oxidation-reduction potential (ORP) is an effective long-term INP performance parameter.

4.6 The environmental toxicology of INPs

NPs are in many of the products that we use on a daily basis and are surreptitiously entering the environment in ever increasing volumes. Although the current mass balance for NPs in the environment system is presently undefined it is conceivable that a large amount of anthropogenic NPs, from an increasing variety of sources, could find their way into the soil, atmosphere and aquatic systems [156].

By association, the concept of deliberately injecting engineered NPs into environmental water systems, albeit as a remedial measure, has consequently attracted scrutiny and concern from both academic and environmental authorities. The same properties that make INPs potentially useful for environmental remediation, specifically their small size and high redox reactivity, also make them potentially harmful to living organisms [157]. To date, a limited number of studies have reported demonstrable toxicity to cells of different types [158–164].

Keenan et al. [164] demonstrated that INPs can rapidly react with oxygen and cause lung cells to die whilst Pisanic et al. [161] observed limited growth and damage in nerve cells exposed to INPs. The primary mechanism for cellular damage is considered to be related to INP oxidation reactions, where redox cycling and the generation of reactive oxygen species (ROS) from reduced Fe within a cell can cause lipid peroxidation and damage to internal structures such as DNA [165–167]. Evidence also suggests INPs to have greater ecotoxicity than nano-scale magnetite [163], highlighting the significant role of reduced iron (Fe^0 or Fe^{2+}) in causing toxic effects. This result also suggests that iron oxides/hydroxides produced by INPs corrosion present significantly less risk, because their inherent nano-toxicity is lower and their increased volume (into the macro-scale) significantly

reduces the likelihood of cellular uptake.

A study by Pisanic et al.[161] showed that INPs with stabilisation coatings, such as polyacrylic acid, resulted in more cellular damage since the particles existed for a longer period without degradation. The shape and size of particles has also been linked to the uptake and toxicology of NPs, with increasingly smaller particles displaying intensifying toxicity.

So far, laboratory 'in vitro' tests have demonstrated INP toxicity on isolated cell cultures and test organisms in sterile deionised water or phosphate buffered saline (PBS) over relatively short timescales (¡1 h), but research using "real" samples and environmentally relevant timescales are extremely limited[148]. It may prove that NPs in natural environments will be less toxic than indicated by laboratory experiments using synthetic parameters. For example, in a study by Tong et al.[168], C60 fullerenes, which in the laboratory have destroyed microbes, were not observed to seriously damage the microbial cultures present in soil after 30 days' exposure.

As the reactions which determine the fate of Fe^0 are well under-stood, the fate of INPs in subsurface and aqueous environments can be reasonably well predicted[169]. The acute redox sensitivity of INPs, which drives the high rates of contaminant reaction and corrosion observed, dictates that their persistence in subsurface environments will be limited. Without fundamentally changing the composition and structure of INPs it is likely that even the most effectively stabilised and engineered INPs are likely to be immobilised in the subsurface via aggregation, mineral sorption or oxidative degradation within timescales in the order of days to weeks. Resultantly, INPs in groundwater is highly unlikely to make it into humans or other mammals as they will have broken down long before contact.

The greatest risk that INPs pose to humans is most obviously during handling, via inhalation and not when it is in the ground. Suitable care and precautions should quite obviously be taken when handling loose, dry INPs but by using the material in the way they are intended i.e. in liquid suspension, any immediate human danger is removed.

Regardless of the performance of INPs for environmental remediation, contaminated sites rely on bioremediation as a concurrent or terminal process and to prevent metal and/or metalloid pollutant re-release[170]. Microbially mediated reactions involving Fe can both aid and hinder aqueous contaminant removal reactions. For example, Fe^{3+} -reducing micro-organisms can reduce and precipitate a wide range of high-valence contaminant metals (such as U, Cr and Tc) through direct enzymatic reduction and via indirect reduction catalysed by biogenic Fe^{2+}, but have also been shown to release a wide range of trace metals formerly bound to Fe^{3+} phases[171].

Preliminary studies using INPs have reported mixed results depending on the chosen experimental parameters. However, most studies using "real" samples at low NP concentrations have reported minimal adverse affect on the functioning of plants, microorganisms and soils[172;173]. Whilst, the chemically reducing conditions imbued by the application of INPs is comparable to the conditions in which anaerobic bacteria develop and proliferate, the capability of micro-organisms to survive in strongly reducing conditions (e.g. 500 to 600 mV) needs further documentation. In addition, mild reducing conditions (e.g. 100 to 300 mV) have been proven as amenable for some anaerobic microbial communities, such as methanogens, but further research is required into

determining the fundamental metabolic pathways involved, including whether soil amendments, such as lactate in soils with insufficient electron donors and/or total organic carbon (TOC) are required [174].

As explained in Section 3.3, the potential re-release of metal and/or metalloid contaminants following a period of apparent remediation is an issue which may significantly limit the extent to which this technology is developed and deployed. There exists a fundamental need to examine the reversible nature of such chemical and/or biological pathways in order to determine appropriate INP physico-chemical composition, complimentary materials/chemicals that may be used in conjunction with INPs and injection procedures that are synergistic to the long-term chemistry and biology of the contaminated site.

4.7 Conclusions - INPs: Yes or no?

As remediation methods need to have non-toxic reaction agents providing long term and stable removal mechanisms, the disadvantages highlighted make it difficult to establish whether this technology, as it currently exists, can be safely applied. Hence, the use of INPs for in situ environmental applications has reached regulated status in many countries, including the USA, Canada, the Czech Republic, Germany, Italy and Slovakia [175]. Other countries, such as the UK, are yet to establish a legislative framework for commercial application. Since the Royal Society and Royal Academy of Engineering 'Nanoscience and Nanotechnologies: Opportunities and Uncertainties' report in 2004 [176] it has been advocated that a "precautionary approach" should be applied to the introduction of engineered NPs to the environment, until further research has been performed on the potential environmental impacts. This recommendation was generic to all types of nano-materials, and also predates a significant amount of the aforementioned studies on the toxicology and environmental fate of INPs. Consequently, in 2010 the UK Department for Environment, Food and Rural Affairs commissioned a literature-based survey to determine "A risk/benefit approach to the application of iron nano-particles for the remediation of contaminated sites in the environment" [177]. The organisation CL:AIRE (Contaminated Land: Applications in Real Environments) was chosen to lead the study. What is considered implicit for the future acceptance of INPs as a remediation technology is a demonstrable and fundamental understanding of INP behaviour in subsurface environmental systems. As part of this, the accurate prediction of INP mobility, reactivity, fate and ecological impact will be critical.

5 Static nano-composites

To avoid the limitations of loose INPs outlined it would be highly advantageous to develop a remediation method that utilizes the reactivity of NPs whilst avoiding the release of free NPs into the environment. One possible route is to develop a 'nano-composite', a product defined as [178];

A multiphase material where at least one of the constituent phases has one dimension less than 100 nm.

Recent research has spawned a multitude of different permutations of nano-composite, where generally the NPs are combined with a micro- or macro-scale support material. In this arrangement the nano-reactivity is

still exhibited and complemented by the properties of the accompanying material.

The remainder of this chapter provides a review of emerging iron and iron oxide containing nano-composites that can be used in static water treatment systems, including permeable reactive barriers, batch reactor systems and point-of-use filters. These systems should avoid the problems associated with uncontrolled NP dispersions by holding them, and sorbed contaminants, securely within a stable structure. Iron and iron oxide NPs [21] are of particular interest because bulk iron has been used in treatment methods for many years and, as a miniscule derivative, INPs have been thoroughly studied for remediation purposes (see Crane and Scott (2012) [10], Zhang [17] and all references therein), although primarily for synthetic laboratory solutions. Most significantly, they have been shown to remediate an impressive range of contaminants [61], from heavy metals via adsorption [2–6;19;50–52;57;58;179–181] to the degradation of chlorinated solvents via chemical reduction [22;27–29;33;148;149], and at much greater rates than bulk iron.

Although this type of technology looks promising, this review will also highlight areas for research and development that require further improvement if nano-composites are to be a viable realistic water clean-up technology. One major issue that becomes apparent within this article is that there is little to no consistency in performance testing for nano-composites developed by different groups. This makes it very difficult to compare products and decide which are the most promising for further funding and upscaling.

As previously discussed, stabilizing NPs with polymers, surfactants and mobile materials has been aimed at improving NP mobility within the subsurface. However, the inherent complexity of natural systems can negate the stabilizing agents which work well in idealized systems and the potential ecotoxicological risks still remain. A more pragmatic solution under investigation is the development of static nano-composites for use in, for example, fixed bed reactors, filter columns, permeable reactive barriers and domestic filters. These micro- to macro-scale structures avoid the problems of the free NPs described above and represent a potential solution by delivering nano-reactivity within a treatment zone (in an environmental or engineered system) but without uncontrolled release of NPs as they are efficiently anchored onto the parent structure.

There are three general categories of static nano-composite; membranes/mats, beads and three dimensional porous structures (Fig. 8). Each of these, and their various benefits and drawbacks for deployment and production, will be briefly addressed in the following sections and summarised in Table 3.

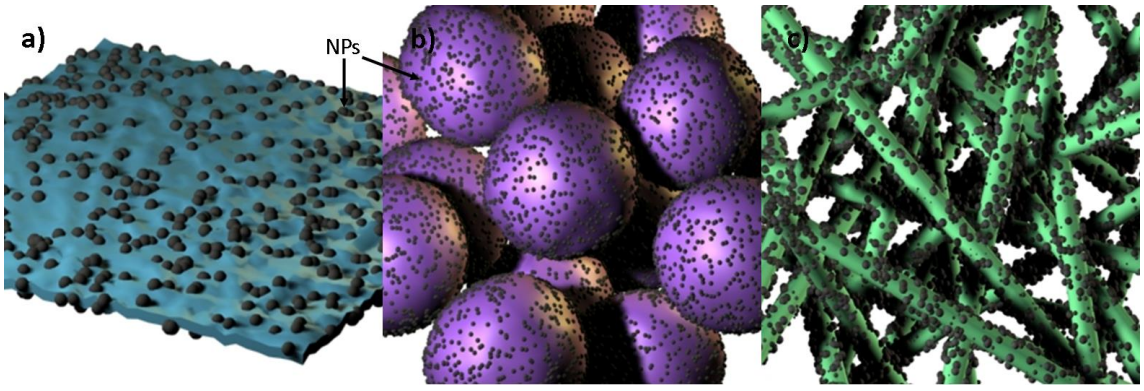

Figure 8: A schematic diagram illustrating the three types of static nano-composite

Table 3: A summary of the three general types of static nano-composites and their advantages and disadvantages

Type	**Advantages**	**Disadvantages**
Membrane	Builds on existing membrane technology for water treatment. Keeps conventional size exclusion properties.	High water pressures can cause membrane to rupture, releasing NPs and contaminants into water system. Cannot be recycled or reused
Beads	Can be easily incorporated into existing infrastructure (e.g. column filters). Water flux can be tailored by altering bead size and packing density.	Reactive material within the core of the bead structure does not come into contact with water and contaminants. Water must flow through channels between beads which generates a high back-flow resistance. Cannot be cheaply recycled or reused without expensive processing.
Porous 3D structures	Avoids limitations of membranes and beads. Size and shape can be tailored to existing infrastructure and flow rate requirements. Good capacity for recycling and reusing the substrate material	Relatively little research has gone into developing such materials.

5.1 Membranes and mats

Membranes traditionally act as size-exclusion based filters, physically preventing harmful microbes or particles from passing through. However, there has been a relativity recent realization that they may be further enhanced by modifying the pores with reactive functional groups and, most recently, NPs. Incorporating NPs into porous micro-filtration membranes is of interest for remediation applications because the membranes offer relatively large pore sizes (50-200nm) and open structures [182]. These properties are important as they allow the immobilized NPs contained within the membrane to be readily accessible for reaction with the aqueous contaminants. This is especially the case if the flow is turbulent and the contact area is high.

The main bulk structure of the membrane is commonly made from polymers such as poly(vinyl alcohol) (PVA) [183–185], poly(acrylic acid) (PAA) [183;185], polyethersulfone (PES) [186] and chitosan [187]. Membrane fabrication methods include phase inversion [186], solution casting [188] and thermal grafting polymerization [182;189]. However the most popular process is electrospinning [183–185;187], where fine fibres are produced by electrostatic repulsion. To incorporate zero-valent INPs, for example, the resulting mat of fibres is then submerged in an aqueous solution of iron salt, where the iron ions complex with the fibres. After rinsing off excess salt, the ions are then chemically reduced, often using sodium borohydride, to form the zero-valent INPs; a relatively cheap and rapid production method.

Using this popular fabrication technique Horzum et al. [187] created a chitosan fibre membrane functionalized with INPs and performed one hour batch experiments to demonstrate the material's ability to remediate As(III) and As(V) from synthetic laboratory solutions of varying concentration and pH. The composite was shown to successfully remove both arsenic species but displayed a better affinity to As(III). The percentage of sorption for both ionic forms reduced with increasing concentrations (range investigated was 0.01-25.0mgL^{-1}) and the material's efficiency was also limited by pH, with As(III) and As(V) sorption decreasing once pH raised above 7 and 8 respectively. Although conceptually successful, the percentage of As(V) removal did not raise over 90% and As(III) removal only peaked above 90% under very specific conditions (pH 3.0 and low concentrations), which can not be guaranteed in real world applications, but may be suitable for certain instances of acid mine drainage. It is also wholly possible that the contact area provided by the composite in these experiments was insufficient to achieve complete As removal.

A more successful nano-composite, fabricated using the same technique, has been developed by a group at Donghua University, China. Crosslinked water-stable electrospun PAA/PVA was used as a nano-reactor to complex Fe(III) with the free PAA carboxyl residues for subsequent reductive formation of INPs [185;190–192]. The resulting polymer nano-fibre mats were stable, highly porous, reusable and able to rapidly remediate waters spiked with Cu(II) and dye. A following study by Ma et al. [183] took the method further by using the electrospun fibres as nano-reactors to prepare core-shell Fe/Pd NPs. By exposing the immobilized INPs on the nano-fibres to Pd(II) solution, bimetallic Fe/Pd NPs were formed via the partial reduction of Pd(II) on the INP surfaces. Batch experiments for the remediation of trichloroethylene (TCE) from synthetic solutions, at relatively low concentrations (10mgL^{-1}), were used to compare the performance of the bimetallic NP composite mats with

colloidal Fe/Pd NPs and mats containing only INPs or Pd NPs. The mat containing just Pd NPs removed only 6.96% of TCE, with the observed uptake attributed to the polymer mat and not the NPs, confirming that the Pd only acts as a catalyst to the degradation reaction. The remaining three samples degraded over 99% of the TCE and reached an equilibrium within 1.5 hours. The mat containing Fe/Pd exhibited the best performance over a range of TCE concentrations (10-100mg^{-1}), presumably because it combined the benefits of the galvanically active bimetallic NPs and polymer mat. Furthermore, varying ionic strength (NaCl 0-1M) and pH (2.5-6.5) caused no significant change in TCE removal, except to show a slightly enhanced efficiency when more acidic.

An equally impressive example for TCE removal by bimetallic NPs in a polymer membrane, is the work of Parshetti and Doong[189]. Using a different fabrication method they were able to immobilize Fe/Ni bimetallic NPs in polyethylene glycol (PEG) grafted membranes. The study functionalized two polymer membranes, polyvinylidene fluoride (PVDF) and nylon 66, with PEG by trapping ferrous and nickel ions via dip coating and thermal grafting polymerization. The ions were subsequently reduced using $NaBH_4$ to create core-shell Fe/Ni NPs uniformly distributed over the membrane surface. The two membranes were then tested and compared for the dechlorination of TCE. The study found nylon 66 to be the most efficient support for TCE degradation because agglomeration was reduced and the nickel content of the bimetallic NPs remained high, both due to the presence of a high density of multifunctional chelating sites. Almost 100% of TCE was removed within 25 minutes and the composite maintained a high reactivity after 10 days during which 16 cycles of injection occurred.

Although these example studies are conceptually successful within a laboratory with synthetic conditions, there are two key factors yet to be addressed; the flow-through tolerance of the composites and their ability to remediate chemically complex environmental waters. A distinct disadvantage of membrane nano-composites is that they can often only tolerate a slow flow rate (less than 1$Lmin^{-1}$) and low water pressure, or else the membrane structure is ruptured and/or destroyed. This reduces the likelihood of realistic application in a domestic setting because flow is simply too slow. Additionally, enforcing flow at a higher pressure, i.e. misusing such a filter, increases the likelihood that the NPs will enter the water supply, thereby creating issues downstream. Therefore, it is vital that flow through experiments are performed to test the structural integrity of any new membrane types over a range of flow conditions.

Daraei et al.[186] developed a novel nano-composite membrane using the phase inversion method. The PES membrane matrix was enhanced with the addition of polyaniline-magnetite (PANI-Fe_3O_4) NPs, where the PANI formed a 8nm thick shell over a 12-28nm iron oxide core. The resulting membrane was tested for the removal of Cu(II) at pH 5. After comparing different compositions, the optimum membrane was with 0.1wt% of NPs present, removing 85% of Cu(II) from a solution of 20mgL^{-1} and 75% from a 5mgL^{-1} solution over 2hrs - eight times more efficient performance than a plain PES membrane. By regenerating the membrane composite with EDTA, it was reusable for 4 cycles, with only 3% loss in Cu(II)adsorption. Unlike the previous examples described above, these contaminant tests were performed in a kinetic system and the pure water flux was examined at 4.5bars trans-membrane pressure. It was found that the better the Cu(II) retention,

the poorer the water flux, with the optimum membrane (0.1wt% of NPs present) having a water flux of only 25kgm^{-2}h^{-1} compared to >>25kgm^{-2}h^{-1} for the pristine PES membrane. It is logical that this occurs; higher flow rates reduce the probability of contaminant removal by reducing the residence time of fluid in the filter. It is also logical that NP-impregnated PES exhibits slower flow-through rates than virgin PES because pore sizes in the membrane are reduced. Although this shows an improved flux rate compared to the previously referenced studies, it is still too low for practical applications. Interestingly, a follow up study was performed to improve the flux to contaminant retention ratio. Daraei et al.[193] investigated how acid functionalized and polymer modified multiwalled carbon nano-tubes (CNT) improved the water flux when blended with the PES membranes. It was found that the membrane containing polycitric acid (PCA) offered the most promising results because the PCA formed dendrimers with carboxyl and hydroxyl groups, leading to super-hydrophilicity in the membrane. The membrane maintained a decent flux durability and reusability during three cycles of fouling-washing steps (Figure 9).

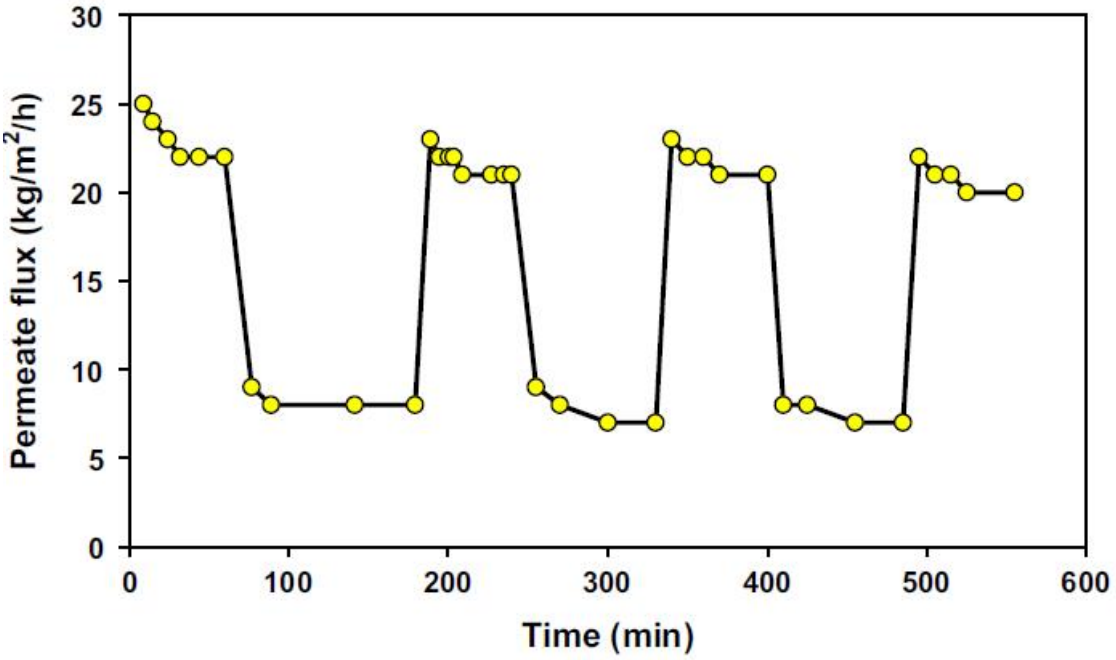

Figure 9: Sequential tests of fouling behaviour of PCA-CNT enforced PES membrane[193]

This study, combined with NP incorporation, represents the next stage of membrane improvement. However, to be suitable for real world applications, there is still the hurdle of complex environmental water chemistry. In the study by Ma et al.[183], mentioned above, tests were performed to investigate NP dissolution over a month - however the tests were performed in pure MilliQ, which is not a realistic representation of a real world water system. Detailed tests analysing the effect of composite aging (corrosion, dissolution, degradation etc.) and clogging in real and complex environmental water samples, and including a suspended particle content, are needed to address this limitation.

5.2 Beads

Bulk nano-composites can also be in the form of micro-/macro-scale beads or particulates. Beads may be utilized in static treatment systems like filter columns (operated in a manner akin to ion exchange columns) and permeable reactive barriers. The key advantage of these spherical nano-composites is that they can be deployed into existing technology and infrastructure, providing few barriers to operational uptake. Multiple studies by C. Noubactep[194–202] have demonstrated the effectiveness of introducing iron into common place sand filter column systems. By doing so the performance is significantly improved and naturally clogs when no reactive iron is left due to the generation of voluminous corrosion products from iron oxidation. By replacing the sand and bulk iron with nano-composite beads, reactivity could be further increased.

Commonly in nano-composite beads the NPs are incorporated into spherical polymer structures and resins, such as chelating resins[203] and ion exchange resins[39;204–207]. A popular example in the literature is the biopolymer alginate[208–216].

Bezbaruah et al. have published an array of studies investigating the entrapment of INPs within calcium (Ca)-alginate beads[209–211]. In each case the composites were fabricated using the same method. Firstly the INPs were synthesized via reduction of an iron salt using sodium borohydride. These were then gently mixed within a solution of sodium-alginate and water, which had been left to stand to ensure no gas bubbles were present. Using a peristaltic pump the mixture was then added drop-wise into a deoxygenated aqueous solution of $CaCl_2$, causing the instant formation of Ca-alginate gel beads containing INPs, which were then dried and hardened. The resulting beads are approximately 5mm in size (Figure 10) and contain NPs with an average size of 35nm and a range of 10-100nm.

Each ensuing study investigated the removal of a different contaminant but under the same physical conditions; i.e. a laboratory made contaminant solution, rotating batch anaerobic reactors, pH not adjusted and samples taken 8 times over 2 hours and in triplicate. To ensure the incorporation of NPs into the beads had not significantly altered their remediative efficiency, the experiments were repeated for free, 'bare' INPs as a comparison. Although the mass of free and entrapped INPs were kept equal within each experiment for consistency, each contaminant required a different amount of the reactive material - presumably based on established literature values. The removal percentages of nitrate (initial concentration range 20mg-100mgL^{-1})[209], TCE (1-40mgL^{-1})[210] and As(V) (1-10mgL^{-1})[211] for the nano-composite beads were approximately 50-73%, 89-91% and 85-100% respectively. The performance for free INPs was shown to be very similar to entrapped NPs in each case. This is an excellent example of a series of logical, repetitive tests where only the contaminant involved is varied. Furthermore, the group has begun to study extra factors that would effect the potential commercialization of the material. For example, shelf-life studies are important because they indicate whether the composite could be stock-piled and transported over extended periods of time and retain the same reactivity. In the 2011 study, Bezbaruah et al.[210] stored beads synthesized from the same batch in a series of air tight vials containing 2% $CaCl_2$ in deoxygenated water, purged with N_2 gas before sealing and wrapping in aluminium to prevent possible photo reactions. Over the course of six months two vials were tested for TCE

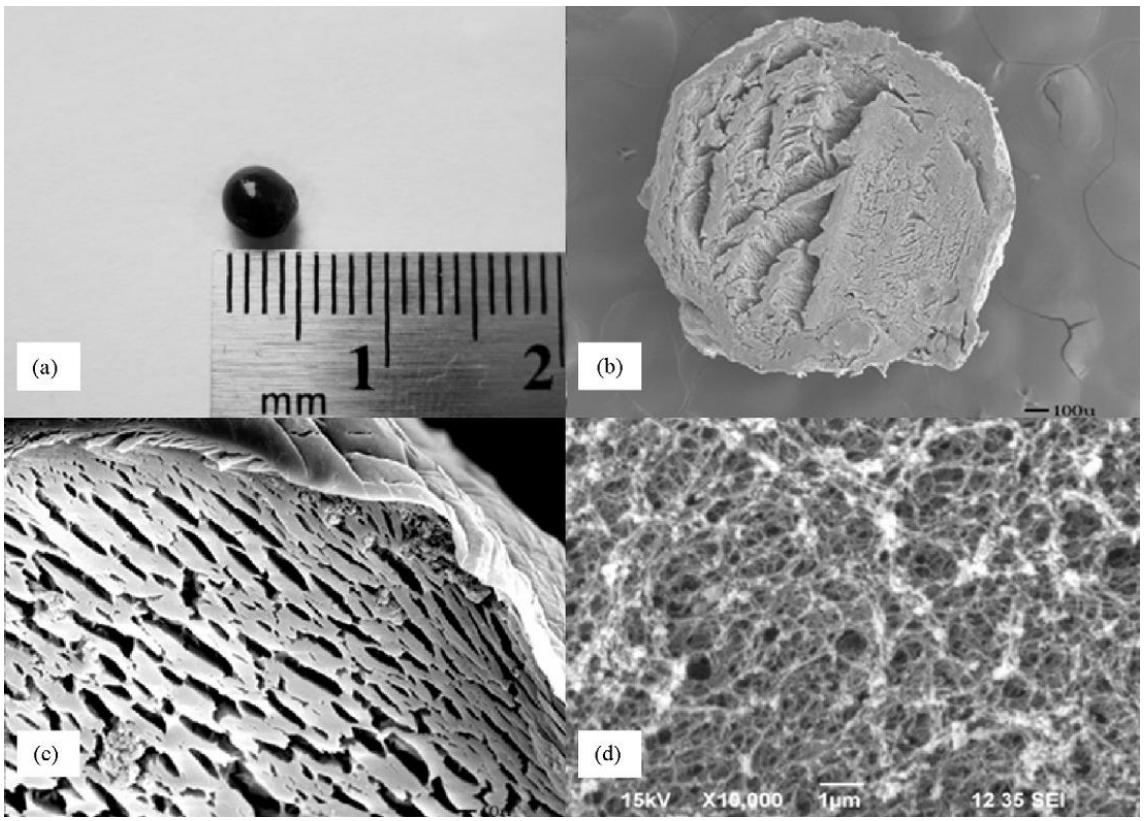

Figure 10: (a) A photograph and (b) SEM image of an alginate bead containing INPs. (c) and (d) SEM images of cross sectioned bead [209]

removal (initial concentration 30mgL^{-}1) every month. The tests revealed that the reactivity began to fall off, albeit marginally, between month 4 and 5, reducing from approximately 89% removal efficiency to 84%. After six months the efficiency was at 82%. Although the investigations are at a relatively early stage, the work so far is an ideal example of logical nano-composite filter development.

As another material alternative, ion exchange resins are also popular for nano-composite beads [39;204–207]. One example in particular reached commercial availability in 2004 [206] under the name of ArsenX^{np}. Since 1997, Lehigh University (Bethlehem, PA, USA) and Bengal Engineering and Science University (Howrah, India) have been working on units to remove arsenic from water in West Bengal, India. Initially, activated alumina was the adsorbent material employed but to improve performance ArsenX^{np} was introduced alongside. The ArsenX^{np} beads, diameter 300 to 1200 μm, contain hydrated ferric oxide NPs within a macroporous anion exchange resin (Fig. 11) [206;217–221] designed to have a high selectivity for sorption of oxyanions of arsenic.

Alongside the material's remediation properties, the success of the product is also due to it's sustainability. The unit (Fig. 12) is attached to hand-pump driven wells, is gravity fed and requires no electricity or pH adjustment. After more than 20000 bed volumes, when an arsenic breakthrough of $50\mu gL^{-1}$ occurs, the product is taken to a central regeneration facility and all arsenic waste removed and safely stored. The success of ArsenX^{np} demonstrates how new, nano-composite materials are emerging commercially and can be easily deployed within already established infrastructure. However, ArsenX^{np} is still a bead nano-composite and therefore suffers from limitations, as outlined below.

Although an advantage of using bead nano-composites in static treatment systems is that the flow rates may

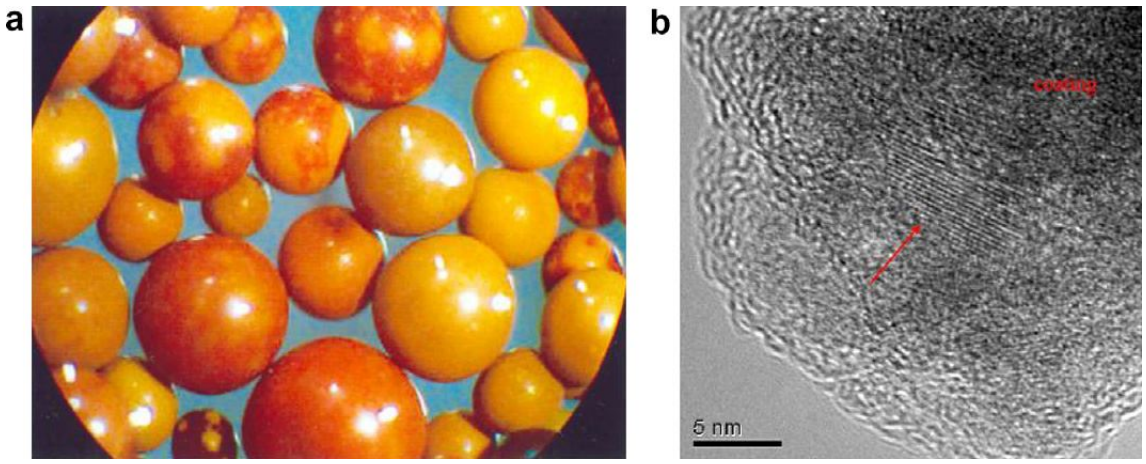

Figure 11: (a) A photograph and (b) TEM image of ArsenX^{np} beads [206]

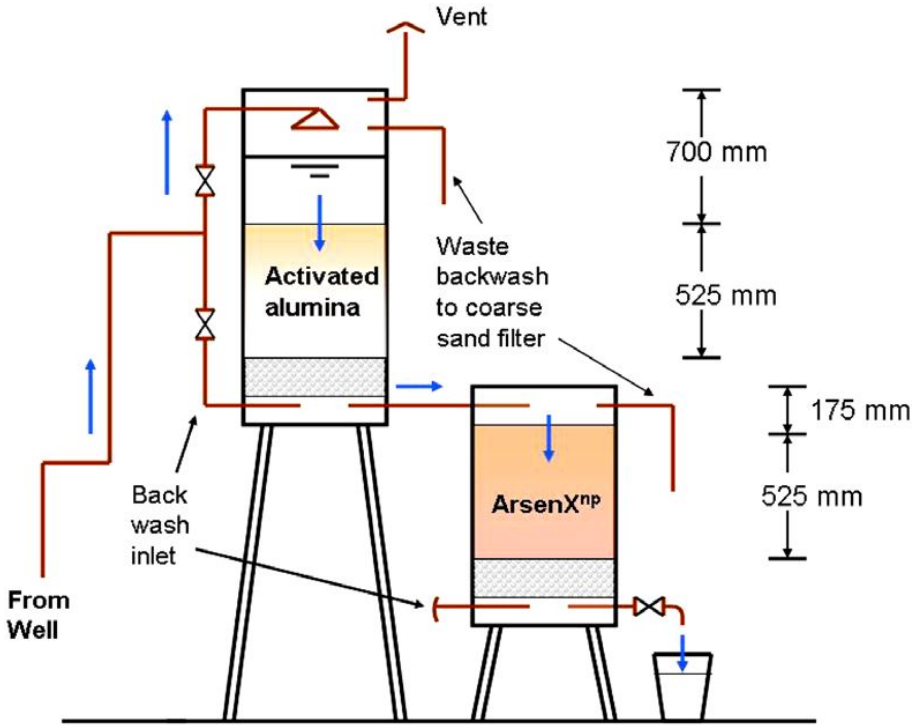

Figure 12: Schematic detail of construction and operation of a split-column unit used in the field [206]

be modified by changing the size and packing density of the beads, water must flow through channels between beads which generates a high back-flow resistance. Furthermore, these products tend to contain a significant mass of wasted reactive material within their volume, which is not afforded the opportunity to react with the water because it is physically entrapped within the structure of the bead and never contacts the polluted water. It may also be argued that they are inefficient on the basis that the overall surface area to volume ratio is poor relative to membranes and foams, making treatment systems potentially larger than necessary, which may be an operational limitation.

5.3 Porous 3D structures - The way forward?

The third and final solution is the incorporation of NPs into 3D porous, continuous, bulk structures. In theory the continuous structure results in limited unreactive volumes and the large structure can be applied to previously established infrastructure such as column filters and permeable reactive barriers. Furthermore, higher flow rates should also be facilitated as the composite maintains the mechanical properties of the parent support. Despite these logical advantages, however, there is relatively little literature covering this topic, especially when compared to the vast array for membrane and bead nano-composites. Amongst the few examples available, support materials include polymers[222;223], graphene[224], carbon glass[225] and chitosan[226].

Savina et al.[223] developed a macroporous polymer containing IONPs (α-Fe_2O_3 and Fe_3O_4), prepared via a simple cryopolymerization process. The NPs were added to a mixture of 2-Hydroxyethyl methacrylate and poly(ethylene glycol)diacrylate and dispersed. Immediately after the addition of ammonium persulfate and tetramethylethylenediamine, the mixture was then placed in a freezer (-12-18°C) for 18 hours. The freezing process separates the water from the NPs, monomer, cross-linker and initiator, to create pockets of ice crystals. Once melted, the crystals leaves behind large interconnected pores of up to 100μm in diameter (Fig. 13).

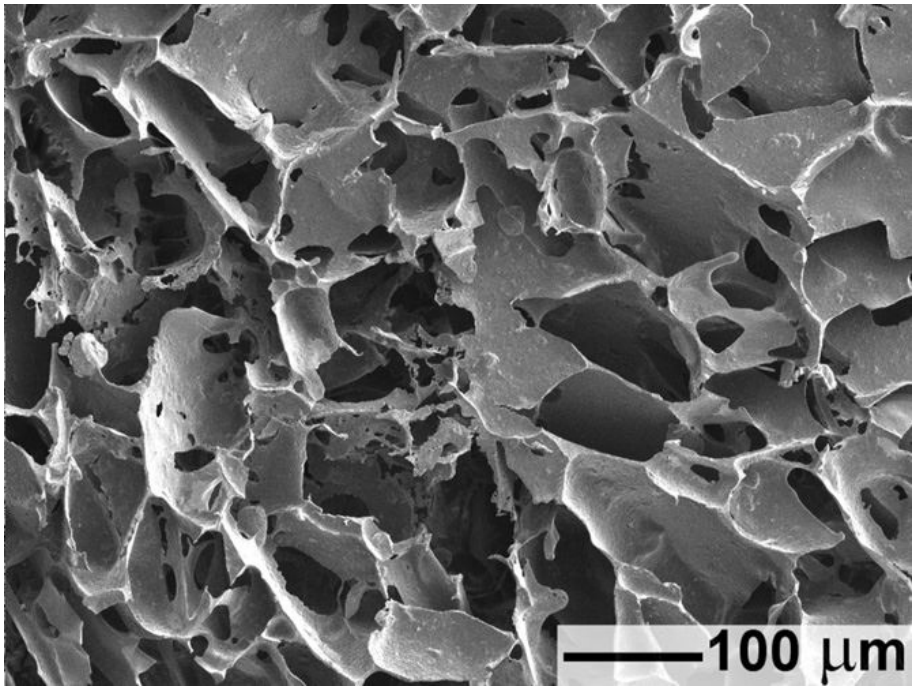

Figure 13: SEM of macroporous polymer containing IONPs[223]

The flow rate (measured at constant hydrostatic pressure of approx. 0.1bar) was 2.29±0.34 and 2.78±0.33 (x10^{-3}) ms^{-1} for the gels containing α-Fe_2O_3 and Fe_3O_4 respectively, when packed in a glass column. This was shown to be very similar to that of gel containing no NPs. This is significantly better than the recommended flow rate for the commercially available ArsenX^{np} beads (described above), which is 5.0x10^{-5} to 1.1$10^{-4}ms^{-1}$ (2040 bed volumes/h) at conventional pressures up to 8bar[221]. The study continued by investigating the adsorption of As(III). Although the removal efficiency was relatively unaffected through the pH range of 3-9, the performance was significantly reduced when compared to free NPs. The equilibrium adsorption capacity

of As(III) for α-Fe_2O_3 and Fe_3O_4 gels was 2.7 and 3.1 mg of As(III) per gram of NPs (or 0.21 and 0.23 As(III)mg/ml of gel) respectively compared to 9.0 and 9.6 mg of As(III) per gram of NPs for free α-Fe_2O_3 and Fe_3O_4 NPs respectively. This significant difference was attributed to the NPs being embedded in the wall of the gel and therefore being less accessible for the contaminant solution (Fig. 14). This result suggests that the reactivity would be improved if the NPs were only on the surface of the parent support and not embedded within it.

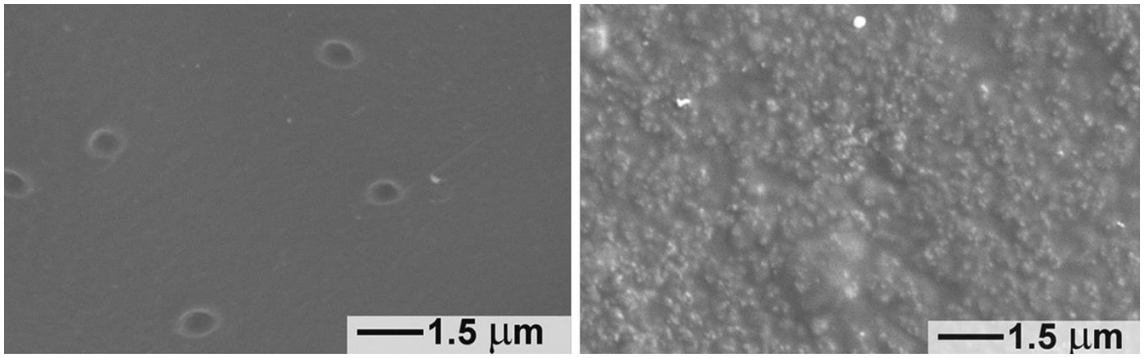

Figure 14: SEM of polymer surface when (a) containing no IONPs and (b) with the IONPs embedded within the surface [223]

Another excellent continuous example is by Sankar et al. [226] who have recently developed a filter system where NPs are embedded within a nano-crystalline metal oxyhydroxide-chitosan structure. Although primarily focused on silver NPs, the work demonstrates how the composite can be easily tailored to the target contaminant in question by simply altering the composition. For example, silver NPs within a AlOOH-chitosan nano-structure removed bacteria and viruses, whilst composites incorporating magnesium oxide NPs within the AlOOH-chitosan nano-structure targeted heavy metals and an FeOOH-chitosan structure was demonstrated for arsenic removal. Furthermore, Sankar et al. [226] developed a point-of-use filter system to incorporate their nano-composite (Fig. 15) - a great demonstration of how such continuous porous structures can be easily incorporated into simple systems. When containing the anti-bacterial composite, the filter demonstrated outstanding results, cleansing 1,500L of water with a bacterial load of 10^5CFU/ml before needing to be replaced or reactivated. Assuming consumption of 10L per day for a family, 120g of composite was estimated to provide safe drinking water for a year at a cost of only $2. Whether a similar performance is seen for other nano-material compositions (such as INPs) is yet to be seen.

Figure 15: The filtration device containing a multilayer axial block within which the tailored composite is placed [226]

The added benefit of such a filtration system is that other nano-composites could be placed within the multilayer axial block to set up a treatment train. This is an ideal example of a set up for performance comparison tests between different continuous composite materials.

Unlike membranes and beads, continuous porous nano-composites can be applied to a wider range of remediation applications. For example, some have been developed to remove oil from water. In order to clean up spills from large volumes of water, ideally a material with superhydrophobicity and superoleophilicity is required.

Calcagnile et al.[222] developed a "white graphene" foam that could float, selectively adsorbing oil from the surface of water. The study used commercial polyurethane foams that, when untreated, are hydrophobic and oleophobic. These foams were then functionalized with- submicrometre polytetrafluroethylene (PTFE) particles and superparamagnetic IONPs via triboelectric charging and deposition respectively. Resultantly the overall synthesis process was simple and the materials inexpensive. It was found that surface morphology and the chemistry of the treated foams affected the adsorption properties and the most efficient foam was created by depositing the NPs before the PTFE. The resulting composite effectively removed the oil and, because of the magnetic properties of the NPs, could then be removed using a magnetic field (Fig. 16).

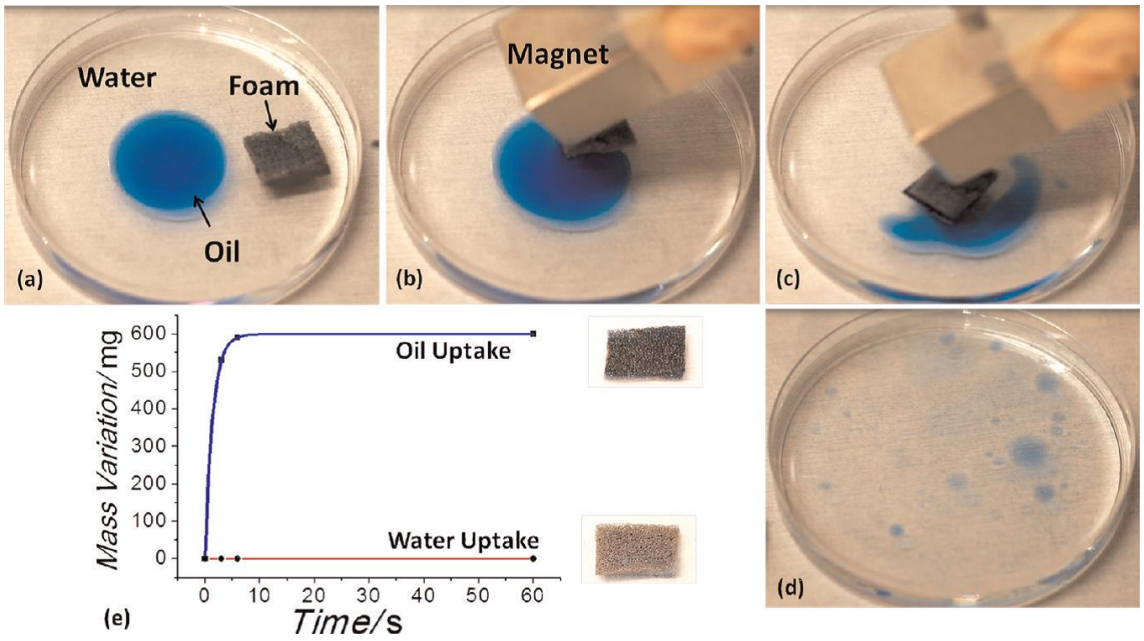

Figure 16: A figure demonstrating the oil adsorption efficacy of IONPs-PTFE functionalized polyurethane foam[222]

Another interesting example is provided by Cong et al.[224] where they developed a graphene/IONP hydrogel. Graphene is an engineered wonder material comprising of sp^2 hybridized carbon atoms and formed with only one atom thickness[37]. Although multiples studies have investigated the potential of graphene as an adsorbent itself[227–233], attention has shifted to creating hybrid materials consisting of both graphene and a coupled nano-material. As large scale production of graphene is still challenging[37], most hybrid composites begin with graphene oxide (GO), which is readily available from natural graphite. GO is ideal for iron compounds that have been shown to cross-link with oxygen groups on activated carbon surfaces. This is because on the surface of GO there are multiple oxygen containing groups, e.g. alcohols, ketones and carboxyl groups. In the study by Cong et al.[224] GO sheets were reduced by ferrous ions, inducing the self-assembly of a graphene hydrogel containing either α-FeOOH nano-rods or magnetic Fe_3O_4 NPs, depending on the pH conditions (Fig. 17). The resulting structure contained interconnecting networks and displayed significant adsorption of oils and heavy metal ions. The synthesis method was also reported to be versatile and adaptable for the production of other graphene hydrogels containing metal oxide NPs.

Although fascinating examples of hybrid materials, these two examples are once again not directly compara-

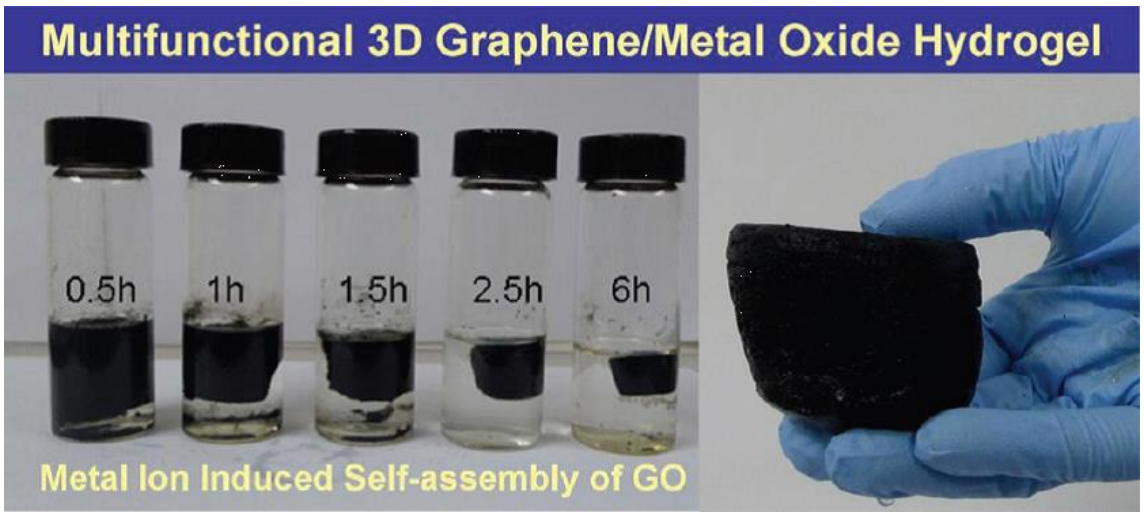

Figure 17: A photo displaying the visual self-assembly of a graphene/iron oxide hydrogel [224]

ble. Tests using the same oil, amount of oil and same weight of reactive materials are required to declare which is the better composite.

As with membranes and beads, these examples of continuous nano-composites have further demonstrated the need for comparative testing. Furthermore, although theoretically superior to other nano-composite structures, the lack of literature and commercially available products potentially indicates a barrier preventing progress for this category of materials. This could possibly be due to cost but also due to practical limitations that need to be overcome such as avoiding the need for compromise between reactivity, flow rate and structural integrity. This is exemplified in the work of Savina et al. [223] who forfeited reactivity for structural integrity.

6 What is holding back static nano-composites?

As can be seen within the literature, an abundance of water remediation technologies exist, both as commercially available products and products undergoing research and development. These include adsorbents, flocculants and coagulants, ion exchange resins and size exclusion filters. As the treated water is often used for drinking, there are multiple stringent regulatory requirements that these technologies must fulfil to achieve commercial maturity and viability.

In the US the quality of drinking water is protected under the Safe Drinking Water Act of 1974 [234] and is regulated by the United States Environmental Protection Agency, the Office of Ground Water and Drinking Water and yet further organizations at a more local level. Also, NSF International, a third-party organization, often plays an important role by certifying all products that come into contact with drinking water, including water filters, chemical treatments and plumbing [235]. In order to gain certification the claims made about a filter's performance must be understood and proved to be true. Furthermore, the NSF Joint Committee on Drinking Water Treatment Units have developed various key standards for evaluation and certification which must be passed depending on the claims made [236].

Meanwhile, within the UK these regulations are outlined and maintained by a combination of authorities -

the Drinking Water Inspectorate (the drinking quality regulator for England and Wales) and Drinking Water Quality Regulator for Scotland, the Health Protection Agency (Department of Health), the Department for Regional Development, the Department for Environment, Food and Rural Affairs (DEFRA), as well as local authorities and water suppliers[237]. The remediation technologies, alongside materials used for storage or transport of water are judged for suitability on the basis of the demonstrable impact they have on the water at the point of consumption - i.e. are there any residual unwanted chemicals appearing?, is the resulting water suitable for human consumption?, etc. The UK Drinking Water Inspectorate releases an annual report detailing which products have fulfilled these conditions and are approved for use in public water supply[238]. This list is purely based on the safety of the drinking water and does not assess the technologies or materials for fitness of purpose.

In all cases the cost of regulatory testing for filter products to be used for drinking water is costly (ranging from $20k minimum to $50k and above) and likely to be prohibitive for individual academics or even universities to take forward. Correspondingly the pathway from promising prototype nano-composite to achieve upscaling and authorization as a market product is likely to be protracted and challenging, requiring one or more rounds of investment.

Nano-composites in particular pose one further problem. Mobile nano-composites are still under scrutiny regarding long term toxicity in the environment and on human health. They are therefore severely limited in commercial applications at the present time. Meanwhile, the more promising bulk nano-composites would need further testing procedures to confirm that no potentially harmful NPs are being released into the drinking water. This may further increase the cost of regulatory testing but is in line with recommendations outlined in the Royal Society report 'Nanoscience and nanotechnologies: Opportunities and Uncertainties'[176].

Furthermore, to be commercially viable, research will need to be pursued to ensure the arising technology is as sustainable as possible. Ideally, to maximise green credentials, the nano-composites should be recyclable, with relatively simple methods available to remove adsorbed contaminants and exhausted NPs and then reuse the substrates. From the resulting NP-contaminant mix desirable metals could then be harvested for further use, therefore providing an economic return, and with the residual waste material needing to be suitably disposed of. Currently, many organisations using NPs follow the traditional chemical safety procedures for 'hazardous materials' throughout the NP life cycle[238]. Although this is a good basis for safely handling and disposing of nano-materials, it would be unsurprising if more specific regulations are drawn up in the future to account for new findings that arise regarding their toxicology. In doing so, would ensure that nano-composites are environmentally friendly throughout their life cycle.

Finally, a key problem, highlighted within this chapter, with the new materials and methods being researched by academia is that there are no standard testing procedures, no set of standardized test pollutants for laboratory experiments and no size requirements for the overall volume of reactive material. Laboratory tests also often overestimate the performance of the product by testing simplistic water systems[10]. This leaves comparison of efficacy very difficult and is currently unsatisfactory for bodies investing in further research and development in this area because it is unclear which product is best.

7 Conclusion

Into the future the viability of the nano-technologies outlined here will be dominated by their scalability, cost of resources and manufacturing, and the ease of use versus other methods. It is therefore unlikely that usage will be widespread and abundant in the near future, although will be highly beneficial for certain niche industrial remediation applications. There also exists the potential for the technology to be successfully coupled with other methods of water treatment forming a modular approach to industrial water treatment that can be tailored to the specific treatment challenge but at low cost. This treatment-train approach may well be where this nano-technology achieves its most significant impact wherein the nano-iron treatment module is plugged into an already existing system.

Is the future of iron nano-particles for water treatment free or fixed? The answer in the long term is that it will likely be both. The injection of 'free' nano-particle suspensions for environmental applications is likely to be used more frequently as a commercial land remediation tool whilst composites for industrial waster treatment are likely to prosper for certain niche applications. Both implementations of the technology remain relatively immature and considerable future developments are likely to arise as commercial interest in the technology persists and operational learning feeds back into the research and development cycles. Whilst the future for nano-iron technology is certainly not fixed, it looks increasingly positive, with the potential to deliver significant worldwide benefit.

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